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EVALUATION OF THE HEATS OF MIXING OF SALT SOLUTIONS FROM IONIC CHARACTERISTICS

I.T. Sryvalin, O.A. Esin, and V.G. Korpachev

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INTRODUCTION

The study of the laws connecting the properties of solutions and their constituent atoms is the central problem of the theory of solutions [1].

Low-temperature solutions, especially solutions of electrolytes in water and other solvents have been the subject of many papers and reviews relating to the solution of this problem. Very little light has been thrown on this question for salt melts, which have no less scientific and practical importance [2]. In what follows we will consider these systems also. Here we will restrict ourselves only to an analysis of the methods of calculating the heat ΔH or energy Q of mixing of binary solutions, assuming [2] that they are connected by the relation [3]:

$$\Delta H = Q \cdot x_1 \cdot x_2 \qquad (1)$$

where x_1 and x_2 are the mole fractions of the components.

1. COULOMBIC INTERACTION

We will deal only with solutions of salts with a common ion. Grim and Herzfeld [4] and then Tobolsky [5] used Born's method to calculate the ionic lattice energy, in order to find the heats of mixing of solid solutions of the alkali metal halides. It was assumed in this that the lattice parameters in mixed crystals (a) are the sum of those for the pure salts (a_1 and a_2), that is, Vegard's empirical rule is obeyed:

$$a = a_1 + (a_2 - a_1) \cdot x \qquad (2)$$

Then the use of Born's simple formula leads to the following expression for the heat of dissolution:

$$\Delta H \simeq -\frac{U}{2} \cdot \left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2 \cdot x_1 \cdot x_2 = K_e \cdot x_1 \cdot x_2 \qquad (3)$$

where U is the lattice energy of one of the salts (or the mean for the two salts), d_1 and d_2 are the sum of the ionic radii of the first and second salts, and K_e is the energy of mixing.

The minus sign is evidence that the process is endothermic, which agrees qualitatively with the results of Delimarskii and Markov [6], according to which binary solutions of most solid salts show positive departures from Raoult's law.

As regards quantitative agreement, Table 1 shows that the energy of mixing $K_e = 4\Delta H$ calculated by Eqn. (3) is considerably less than that found experimentally (Q_{expt}).

Equation (3) is not applicable to melts, since Vegard's rule does not hold for them. A more suitable assumption here is that of Förland [7], who assumed that ions are rigid spheres and the distances between neighbours of opposite charge are unchanged on mixing the molten salts. He considers that the heat of mixing originates in the circumstance that the energy of the coulombic repulsion between the nearest cations (when the anion is common) in the solution ($X^+-Z^--Y^+$) differs from half the sum of those for the pure salts ($X^+-Z^--X^+$) and ($Y^+-Z^--Y^+$). Neglecting the

TABLE 1. Energy of mixing for solid solutions of certain salts.

System	Constituent energies of interaction		Energy of mixing		Reference
	K_e (Tobol'skii)	K_L (Lumsden)	$Q = K_e + K_L$	Q_{exp}	
KCl—RbCl	0.4	0.4	0.8	0.81	8,9
KCl—KBr	0.4	0.60	1.00	0.92	8,9
NaCl—NaBr	0.60	0.72	1.32	1.36	9,10
KBr—KI	1.00	0.40	1.40	1.56	8
NaBr—KBr	2.20	0.80	3.00	2.80	11
NaI—KI	2.00	0.60	2.60	2.50	11
NaCl—KCl	2.80	1.20	4.0	4.20	11,12
AgCl—LiCl	4.80	4.0	8.80	8.80	13
AgBr—LiBr	4.4	3.0	7.40	7.52	14
AgBr—NaBr	1.2	2.0	3.20	4.20	14
$MgCl_2$—LiCl	0	0	0	0	15
$PbBr_2$—$ZnBr_2$*	4.8	0	4.0	3.6	16
$PbBr_2$—$PbCl_2$*	0.4	0.4	0.8	—1.2	17
KBr—RbBr*	0.4	0.4	0.8	0.60	18
RbCl—RbBr*	0.4	0.4	0.8	0.8	18
KCl—KBr*	0.4	0.60	1.00	0.8	18
KCl—RbCl*	0.4	0.4	0.8	0.60	18

influence of subsequent layers, he obtained for an equimolecular melt:

$$\Delta H \simeq \frac{U}{4}\left(\frac{d_1-d_2}{d_1+d_2}\right)^2 \cdot x_1 \cdot x_2 = \frac{U}{4} \cdot \delta^2 \cdot x_1 \cdot x_2 = K_e'' \cdot x_1 \cdot x_2 . \quad (4)$$

Comparison of expressions (3) and (4) which in general are similar in form, shows that the heats of mixing in them differ in sign and also that ΔH for solid solutions is twice that for liquid solutions. Experiment shows that in accordance with Eqn. (4) heat is liberated ($Q_{expt} < 0$) in several instances, namely in the mixing of molten alkali metal halides (see Tables 2 and 3). However, the calculated energies of mixing ($K_e'' = 4\Delta H$) sometimes differ considerably from the experimental values. For molten salts with a common cation the comparison with published data [19,20] shows a still greater discrepancy in the values of Q.

True, in measuring the heats of mixing of molten alkali metal nitrates, Kleppa and Herch [26] found (see Table 4) that they are satisfactorily described by Förland's approximation:

$$\Delta H \simeq x_1 \cdot (1 - x_1) \cdot U \cdot \left(\frac{d_1-d_2}{d_1+d_2}\right)^2 = x_1 \cdot x_2 \cdot U \cdot \delta^2 . \quad (5)$$

This cannot be said about solutions of silver or thallium nitrates with alkali metals nitrates, for which they [27] propose a somewhat different semi-empirical expression:

$$\Delta H = -x_1 \cdot x_2 (140 \cdot \delta^2 - U'' \cdot \delta) . \quad (6)$$

In this, the first term inside the parentheses allows for the electrostatic interaction (coulombic repulsion) and the second, the presence of a covalent constituent in the lattice energy of $AgNO_3$ and $TlNO_3$.

As Table 5 shows, by a suitable choice of the parameter U'' (different for $AgNO_3$ and $TlNO_3$) satisfactory agreement was reached between the values calculated by formula (6) and the experimental data.

Blander [29] made an attempt to improve Förland's equation, by allowing for the coulombic forces being far-acting. However, he was restricted to the solution of only the linear problem for a dilute binary solution of salts with a common anion.

By considering a linear series of n cations of the solvent (at a distance r from one another), in which cations of

TABLE 2. Energies of mixing for molten alkali metal halides.

System	Contribution of individual effects to the energy of the solution				Calculated energy of mixing, $Q = (K_P + K_L)$	Q_{exp} (Ref. 35)	Reference
	$-K_P$ (Lumsden)	K_L (Lumsden)	$-K_e'$ (Blander)	$-K_e''$ (Förland)			
LiF—NaF	1.8	0.2	0.6	1.0	—1.6		
LiF—KF	5.6	1.4	1.5	4.3	—4.2	—4.0 (—4.8)	21
LiF—RbF	7.3	2.8	2.0	5.9	—4.5	—4.2	
LiF—CsF	9.0	5.3	2.7	8.0	—3.7	—3.5	
NaF—KF	1.1	0.7	0.5	1.1	—0.4	—0.4	
NaF—RbF	1.8	1.7	1.2	2.0	—0.1	—0.2	
NaF—CsF	2.8	3.7	1.8	3.4	+0.9		
KF—RbF	0.1	0.2	0.1	0.15	+0.1		
KF—CsF	0.4	1.5	0.17	0.6	+1.1		
RbF—CsF	0.1	0.5	0.07	0.2	+0.4		
LiCl—NaCl	1.2	0.1	0.4	0.5	—1.1		
LiCl—KCl	4.4	0.4	1.2	2.4	—4.0	—3.5 (—4.0)	21
LiCl—RbCl	5.8	1.2	1.7	3.4	—4.6		
LiCl—CsCl	8.1	2.2	2.1	4.6	—5.9	—5.0	
NaCl—KCl	1.1	0.3	0.4	0.7	—0.8	—0.8	
NaCl—RbCl	1.8	0.7	1.0	1.0	—1.1		
NaCl—CsCl	3.2	1.5	1.6	2.0	—1.7		
KCl—RbCl	0.1	0.1	0.08	0.1	0.0		
KCl—CsCl	0.6	0.5	0.17	0.4	—0.1		
RbCl—CsCl	0.2	0.2	0.07	0.11	0		
LiBr—NaBr	1.0	0.0	0.35	0.46	—1.0		
LiBr—KBr	3.8	0.4	0.65	2.0	—3.4	—3.0 (—3.2)	21
LiBr—RbBr	5.3	0.9	0.85	2.9	—4.4		
LiBr—CsBr	7.7	1.8	1.1	3.9	—5.9		
NaBr—KBr	1.0	0.2	0.3	0.6	—0.8	0	
NaBr—RbBr	1.8	0.6	0.4	1.1	—1.2		
NaBr—CsBr	3.2	1.3	0.7	1.8	—1.9		
KBr—RbBr	0.1	0.1	0.1	0.008	0.0		
KBr—CsBr	0.6	0.5	0.25	0.35	—0.1		
RbBr—CsBr	0.2	0.2	0.1	0.1	0.0		
LiI—NaI	0.9	0.0	0.3	0.36	—0.9		
LiI—KI	3.5	0.3	0.5	1.6	—3.2		
LiI—RbI	5.0	0.6	0.6	2.3	—4.4		
LiI—CsI	7.1	1.2	0.9	3.2	—4.9		
NaI—KI	0.9	0.1	0.2	0.5	—0.8	—0.7	
NaI—RbI	1.7	0.4	0.3	0.9	—1.3		
NaI—CsI	3.0	0.9	0.5	1.5	—2.1		
KI—RbI	0.2	0.1	0.06	0.06	—0.1		
KI—CsI	0.6	0.3	0.2	0.3	—0.3		
RbI—CsI	0.2	0.1	0.06	0.1	—0.1		

TABLE 3. Energy of mixing for molten salt solutions with a common cation.

System	Constituent energies of mixing		Energy of reaction		Reference
	K_e'' (Förland)	K_L (Lumsden)	$Q = K_e'' + K_L$	Q_{exp}	
NaCl—NaBr	—0.60	0.72	+0.12	0	22–24
NaCl—NaI	—2.40	1.60	—0.8	—0.8	25
KCl—KI	—1.60	1.20	—0.4	—0.8	25
KCl—KBr	—0.40	0.60	+0.2	0	22,24
RbCl—RbBr	—0.40	0.40	0		
AgCl—AgBr	—0.40	0.40	0	0	24
$PbBr_2$—$PbCl_2$	—0.40	0.40	0	—1.2	17
KBr—KI	—1.00	0.4	—0.60		

TABLE 4. Comparison of experimental and calculated energies of mixing, for equimolar solutions of molten alkali metal nitrates.

Melts	Contribution of individual constituents to the energy of mixing			Energy of mixing		Q_{exp} (Ref. 26)
	K_P (Lumsden)	K_L (Lumsden)	K_e'' (Förland)	$Q = K_P + K_L + K_e''$	$Q = -140\delta^2$ (Kleppa)	
$LiNO_3$—$NaNO_3$	—0.44	0.03	—0.12	—0.53	—0.49	—0.464
$LiNO_3$—KNO_3	—1.74	0.08	—0.15	—1.81	—1.82	—1.76
$LiNO_3$—$RbNO_3$	—2.26	0.20	—0.25	—2.31	—2.5	—2.47
$LiNO_3$—$CsNO_3$	—2.94	0.40	—0.30	—2.84	—3.5	—3.0
$NaNO_3$—KNO_3	—0.39	0.04	—0.06	—0.41	—0.45	—0.41
$NaNO_3$—$RbNO_3$	—0.75	0.09	—0.08	—0.74	—0.79	—0.75
$NaNO_3$—$CsNO_3$	—1.03	0.25	—0.20	—0.98	—1.4	—1.04
KNO_3—$RbNO_3$	—0.05	0.01	—0.02	—0.06	—0.05	—0.06
KNO_3—$CsNO_3$	—0.15	0.02	—0.05	—0.18	—0.27	—0.1
$RbNO_3$—$CsNO_3$	—0.05	0.01	—0.02	—0.06	—0.10	—0.014

TABLE 5. Energy of mixing of molten alkali metal nitrates and bromides with silver and thallium salts.

Melts	Contribution of individual constituents to the energy of the solution, calculated by formulae: K_P (19)	K_L (17)	K_e (4)	K_c (21)	$Q = K_P + K_L + K_e + K_c$	$Q = -140\delta^2 + U^0\delta$	Q_{exp}	Reference
$LiNO_3$—$AgNO_3$	−0.72	0.16	−0.13	+1.50	+0.81	+0.79	+0.65	27
$NaNO_3$—$AgNO_3$	−0.12	0.09	−0.03	+0.72	+0.66	+0.55	+0.59	27
KNO_3—$AgNO_3$	−0.04	0	−0.02	−0.45	−0.51	−0.52	−0.45	27
$RbNO_3$—$AgON_3$	−0.12	0.01	−0.02	−0.85	−0.96	−1.08	−1.19	27
$CsNO_3$—$AgNO_3$	−0.3	0.07	−0.05	−1.40	−1.43	−2.0		
LiBr—AgBr	−0.75	0.18	−0.15	+2.52	+1.80	+1.72	+1.88	14,28
NaBr—AgBr	−0.12	0.10	−0.03	+1.14	+1.09	+0.98	+1.05	14
KBr—AgBr	−0.05	0	−0.02	−0.72	−0.79	−0.78	−1.48	14
RbBr—AgBr	−0.15	0	−0.03	−1.35	−1.53	−1.58	−2.58	14
CsBr—AgBr	−0.33	0.08	−0.06	−2.18	−2.49	−2.79		
$LiNO_3$—$TlNO_3$	−2.5	0	−0.2	+1.92	−0.78	−0.71	−0.88	27
$NaNO_3$—$TlNO_3$	−0.65	0	−0.07	+1.07	+0.35	+0.30	+0.256	27
KNO_3—$TlNO_3$	−0.08	0	−0.04	+0.60	+0.48	+0.38	+0.44	27
$RbNO_3$—$TlNO_3$	−0.02	0.06	−0.07	+0.27	+0.23	+0.23	+0.232	27
$CsNO_3$—$TlNO_3$	0	0.10	−0.01	−0.18	−0.1	−0.15		

another kind are distributed — at a distance $(1+\gamma)r$ from another — he finds the following expression for measurement of the energy of coulombic repulsion:

$$\Delta E = -\frac{e^2}{r}\left[2\sum_1^\infty \frac{1}{n+\gamma}\cdot(-1)^n - (1+2\gamma)\cdot\sum_1^\infty \frac{1}{n+2\gamma}(-1)^n - \left(\frac{1-\gamma}{1+\gamma}\right)\cdot\sum_1^\infty \frac{1}{n}\cdot(-1)^n\right], \quad (7)$$

where e is the charge of an electron.

ΔE is always negative and approximately 40% less in absolute value than that calculated by Förland's formula. As Table 2 shows (K'), the agreement with experiment is not improved.

2. CALCULATION OF OTHER TYPES OF INTERACTION

Some authors [10,30], following Mayer and Born [31,32], used an expression for the lattice energy allowing for the intermolecular interaction:

$$-U = -\frac{\alpha}{r} - \frac{c}{r^6} + B(r), \quad (8)$$

which includes the coulombic, van der Waals, and Born-type (repulsive) interactions. They neglected null energy and multipolar interaction. If the lattice parameters of the pure components and of the equimolecular solution are denoted r_1, r_2, and $r_{1,2}$, then the change in coulombic energy is:

$$\Delta U_{coulomb} = \frac{2\alpha\cdot e^2}{r_{1,2}} - \frac{\alpha\cdot e^2}{r_1} - \frac{\alpha\cdot e^2}{r_2}, \quad (9)$$

where α is the Madelung constant.

By assuming that the distribution of the cationic and anionic sites is random [4], Wallace finds the following relation between the constants of the van der Waals interaction ($c_{i,j}$) of the salts and the overall constant (c) for the solution:

$$c = N_1\cdot N_2\cdot c_{1,2} + N_1\cdot N_4\cdot c_{1,4} + N_2\cdot N_3\cdot c_{2,3} + \frac{1}{2}(N_1^2\cdot c_{1,1} + N_2^2\cdot c_{2,2} + N_3^2\cdot c_{3,3} + N_4^2\cdot c_{4,4} + 2N_1\cdot N_3\cdot c_{1,3} + 2N_2\cdot N_4\cdot c_{2,4}). \quad (10)$$

Here N_1 and N_3 are the ionic fractions of cations 1 and 3, and N_2 and N_4 those of the anions 2 and 4.

According to Mayer and coworkers [31,33], for the alkali metal halides:

$$B(r) = b\cdot c_{i,j}\cdot e^{\frac{r_i+r_j}{\rho}},$$

where r_i and r_j are the ionic radii, $\rho = 0.345\times10^{-8}$ cm, $b = 1\times10^{-12}$ erg; for the cations $c_{i,j} = c_1 = 1.25$; for the anions $c_{i,j} = c_2 = 0.75$, and for particles with opposite charges $c_{i,j} = c_{1,2} = 1.0$.

The potential of repulsion $B(r_0)$ for solid solutions was evaluated with allowance for the interaction of the central ion with z nearest neighbours and z' ions of the following coordination sphere:

$$B(r_0) = \beta_1\cdot e^{-r_0/\rho} + \beta_2\cdot e^{-ar_0/\rho} \quad (11)$$

where

$$\beta_1 = b\cdot z\cdot c_0\cdot\left[N_1\cdot N_2\cdot e^{\frac{r_1+r_2}{\rho}} + N_1\cdot N_4\cdot e^{\frac{r_1+r_4}{\rho}} + N_2\cdot N_3\cdot e^{\frac{r_3+r_2}{\rho}}\right] \quad (12)$$

$$\beta_2 = \frac{b\cdot z'}{2}\left[c_1\cdot\left(N_1^2\cdot e^{\frac{2r_1}{\rho}} + 2N_1\cdot N_3\cdot e^{\frac{r_1+r_3}{\rho}} + N_3^2\cdot e^{\frac{2r_3}{\rho}}\right) + c_2\left(N_2^2\cdot e^{\frac{2r_2}{\rho}} + 2N_2\cdot N_4\cdot e^{\frac{r_2+r_4}{\rho}} + N_4^2\cdot e^{\frac{2r_4}{\rho}}\right)\right] \quad (13)$$

c_0 is the van der Waals constant, taking into account the interaction between ions of opposite charge; c_1 is the same for intercationic, and c_2 that for interanionic, interactions.

The value of r_0 is the equilibrium distance between the nearest neighbours, whereas ar_0 up to the second coordination layer, and r_1, r_2 etc. are characteristic parameters of individual types of ions.

In Eqns. (11)–(13) the interaction between a given pair of ions in a solution is identical with that in the pure salts at corresponding distances.

Table 6 shows the experimental lattice parameters of solid solutions of the NaCl–NaBr, KCl–KBr, and RbCl–KCl binary systems, together with the repulsion constants β and van der Waals constants c, calculated [10] by Eqns. (11)–(13). In this, the equilibrium distances r_0 in the solid solution at 0°K were evaluated with the aid of the Born–Mayer relation:

$$r_0\left(\frac{dU(r_0)}{dr}\right) = \frac{3T}{N\cdot\varepsilon}\left(\frac{dV}{dT}\right)_p, \quad (14)$$

where ϵ is the compressibility.

Furthermore, the values of r_0 were calculated by the additivity rule and appeared (see Table 6) quite close to the experimental values.

The heat of mixing ΔH is expressed by the lattice energies U_1, U_2, and U of the pure salts and solid solution:

$$\Delta H = U - x_1\cdot U_1 - x_2\cdot U_2. \quad (15)$$

TABLE 6. Lattice parameters of solid solutions of alkali halides, repulsion constants (β_1 and β_2), and van der Waals forces (c) after Wallace [10].

System	Mole fraction, N_1	$10^8 r_{0}$, cm (298°K) expt.	by the rule of mixing	deviation	$10^8 r_{0}$, cm (0°K) expt.	by the rule of mixing	deviation	$10^{60} c$, erg cm	$10^{12}\beta_1$, erg	$10^{12}\beta_2$, erg
NaCl—NaBr	1.0	2.8144	—	—	2.79	—	—	180	5498	24880
	0.75	2.8588	2.8560	0.0028	2.837	2.831	0.006	201	6081	30170
	0.50	2.9017	2.8977	0.040	2.88	2.872	0.008	223	6664	35990
	0.25	2.9411	2.9393	0.038	2.919	2.913	0.006	247	7247	42340
	0.0	2.9809	—	—	2.954	—	—	271	7830	49230
KCl—KBr	1.0	3.1362	—	—	3.105	—	—	451	13380	30480
	0.75	3.176	3.176	0.000	3.151	3.146	0.006	488	14840	35840
	0.50	3.217	3.216	0.001	3.192	3.184	0.008	325	16300	41730
	0.25	3.257	3.256	0.001	3.229	3.224	0.005	564	17760	48240
	0.0	3.2952	—	—	3.263	—	—	604	19220	55240
KCl—RbCl	1.0	3.1362	—	—	3.105	—	—	451	13380	30480
	0.5	3.216	3.211	0.005	3.185	3.178	0.07	570	16590	34360
	0.0	3.286	—	—	3.251	—	—	692	19790	39060

TABLE 7. Comparison of the lattice energies and heats of mixing, and also of their constituents for solutions of salts which form solid solutions (kcal mole^{-1}).

System	N_1	Repulsion potential $B(r_0)$ 298°K abs.	298°K rel.	0°K abs.	0°K rel.	Coulombic energy $-\frac{\alpha e^2}{r_0}$ 298°K abs.	298°K rel.	0°K abs.	0°K rel.	Intermolecular interaction $-\frac{c}{r^6}$ 298°K abs.	298°K rel.	0°K abs.	0°K rel.	Lattice energy, $-U$ 298°K	0°K	Heat of mixing 298°K	0°K	298°K	0°K
														absolute values		Refs. 9 and 10		calculated (Ref. 34)	
NaCl—NaBr	1.0	26.22		28.21		200.7		202.5		5.23		5.52		179.71	179.81				
	0.5	24.88	0.04	26.53	—0.331	194.7	0.4	196.2	0.7	5.37	0.015	5.64	0.05	175.19	175.31	0.34	0.54	0.45	0.42
	0.5	(25.18)	(0.34)	(27.20)	(0.32)	(195.6)	(0.1)	(196.7)	(0.2)	(5.35)	(0.035)	(5.64)	(0.05)	(175.17)	(175.14)			(0.47)	(0.57)
	0	23.46		25.54		189.5		191.3		5.54		5.86		171.58	171.62				
KCl—KBr	1.0	22.90		25.08		180.3		182.0		6.89		7.25		164.29	164.17				
	0.5	22.07	0.27	23.74	—0.2	177.0	0.2	177.0	0.6	6.85	0	7.225	0.086	160.48	160.48	0.23	0.45	0.47	0.49
	0.5	(22.12)	(0.32)	(24.31)	(0.36)	(177.4)	(0.1)	(177.4)	(0.2)	(6.84)	(0.01)	(7.20)	(0)	(160.52)	(160.29)			(0.43)	(0.56)
	0	20.71		22.83		173.2		173.2		6.81		7.152		157.68	157.52				
KCl—RbCl	1.0	22.90		25.08		180.3		182.0		6.89		7.25		164.29	164.17				
	0.5	22.29	0.04	24.44	0	177.4	0.35	177.4	0.5	7.4	—0.005	7.92	—0.06	160.91	160.88	0.20	0.40	0.39	0.44
	0.5	(22.67)	(0.42)	(24.95)	(0.50)	(177.8)	(0.1)	(177.8)	(0.1)	(7.39)	(0.005)	(7.85)	(0.01)	(160.22)	(160.7)			(0.57)	(0.61)
	0	21.60		23.93		173.8		173.8		7.9		8.46		158.3	158.33				

In the opinion of Wallace, the change in $B(r)$ is approximately two-thirds of the energy of mixing; the change in the coulombic energy covers most of the rest, and the van der Waals force makes a small contribution.

Table 7 gives the lattice energies, the values of the individual constituents, and their contributions to the heat of mixing, calculated[34] by Eqns. (6)–(15). The calculated values of ΔH are compared with those found experimentally. Although our calculated values do not differ too much from Wallace's values, the relative significance of the various types of interaction is different. The main source of ΔH is the change in the coulombic interaction and not the repulsion forces. Both types of energy are very sensitive to the departure of the lattice parameters from additivity. Values calculated assuming that Vegard's law is applicable are given in parentheses. Here the relative significance of the change in the Born repulsion has increased to about three-quarters of the total energy of mixing. However, in all the systems there are positive departures from Vegard's law. This leads to a relative decrease in the energy of coulombic interaction, and consequently an increase in the positive contribution to the heat of mixing. On the other hand, the Born potential here falls, its contribution decreases, and even the sign changes to positive (at 0°K).

It is interesting to note that the results of the calculation are almost independent of whether we use the equilibrium values of the lattice parameters or assume the applicability of the additivity rule. However, this is correct only when allowance is made not only for the coulombic interaction but also the potential of repulsion.

Comparison with experiment shows a systematic increase in the calculated values of ΔH. Allowance for only one coulombic interaction at 298°K gives the best agreement with experiment, which cannot be said of the data for 0°K.

Wallace's method is apparently not applicable to liquid salts, since there is no long-range order in them. Lumsden[35] considered solutions of molten alkali metal halides with a common anion. He assumes that the energy of mixing is due above all to the asymmetry of the electric field of cations of different kind. The main negative contribution is therefore introduced by the polarisation energy; the increase in van der Waals interaction is a positive term.

Lumsden neglects the change in coulombic energy, which is scarcely proved. The method of calculation proposed by him is scarcely applicable to solutions of salts with a common cation.

The non-polar London forces which act between ions give an energy contribution which is inversely proportional to the distance raised to the sixth power. The forces are short-range, therefore in a mixture with a common anion they can be restricted to the interaction between the nearest cations.

Starting from the simplest geometrical relations, Lumsden finds an expression for the change in the energy of the non-polar interaction for mixing:

$$E_L = K_L \cdot \frac{x \cdot y}{x + y} \qquad (16)$$

Here x and y are the number of moles of the salts X^+Z^- and Y^+Z^-; but the quantity K_L is connected with the constants $c_{i,i}$ by the relation:

$$K_L = 86.5 \cdot \left[\frac{c_{X,X}}{(2r_{X,Z}^2)^3} + \frac{c_{Y,Y}}{(2r_{Y,Z}^2)^3} - \frac{2\sqrt{c_{X,X} \cdot c_{Y,Y}}}{(r_{X,Z}^2 + r_{Y,Z}^2)^3} \right] \qquad (17)$$

We note that the values E_L calculated by Wallace's formulae are considerably less than those for the same salts by Eqn. (17). The main reason for this is the different definition of the constant $c_{i,j}$ for the mixture of salts. Whereas Lumsden assumes that $c_{X,Y}^2 = c_{X,X}\, c_{Y,Y}$, the quantity $c_{X,Y}$ found by formula (10), differs little from the arithmetic mean.

The rule of the geometric mean, true under definite conditions for a series of simple mixtures of dielectrics cannot be unconditionally applicable to ionic solutions. The introduction of formula (10) here is more reasonable.

As is well-known, the geometric mean is always less than the arithmetic mean or equal to it. Therefore the results of the calculations by Eqns. (16) and (17) should

give an increased positive departure in the heat of mixing. Allowance for the asymmetry of the electric field in mixtures with a common anion leads to the following expression for the polarisation energy:

$$E_P = K_P \cdot \frac{x \cdot y}{x + y} \qquad (18)$$

$$K_P = -1060 \cdot N \cdot \alpha \left(\frac{1}{r^3_{X,Z}} - \frac{1}{r^3_{Y,Z}} \right)^2 \qquad (19)$$

In this the molar polarisability $N\alpha$ is expressed in cm^3 but the inter-ion distance $r_{i,j}$ in ångströms (10^{-8} cm).

Table 2 gives the values of the constants K_L and K_P calculated by Lumsden for mixtures of alkali halides with a common anion. In this, the inter-ionic distances were taken from Wyckoff[36], the constants $c_{i,j}$ from Mayer[32], and the data on polarisabilities from Kordes[37]. According to Lumsden, the quantities he obtained agree with the thermal analyses for several binary systems.

Lumsden evidently overestimates the size of the contribution of polarisation in the energy of mixing. The linear model of the solution can hardly be transferred to the three-dimensional without some restrictions†.

It is necessary to consider also the possible revaluation of the role of the London interaction. Use of the geometric mean rule for the constants $c_{i,j}$ leads, evidently, to too high results. On the other hand, allowance for the non-polar interaction, although small, is very important, especially in mixtures with a common cation. In several instances the London forces are the only ones making a positive contribution to the heat of mixing.

As the electron clouds of the ions can be deformed and partially overlap one another, a considerable part of the contribution to the excess energy of the mixture is due not only to the repulsion of particles with charges of the same sign, but also to the change in the interaction of the cation with the anion. The mean distance between them is determined by the minimum free energy — see Eqn. (14) — and should change on mixing.

We will restrict discussion to the formulae mentioned and will not consider those in which the energies of mixing are linked with macroscopic characteristics. This refers in particular to Shimoji's equation[38], in which molecular volumes are introduced instead of the ionic distances.

3. COMPARISON WITH EXPERIMENTAL DATA

To calculate the energies of mixing we used the usual values of the ionic radii, which are compromises between those recommended by various authors. Where possible, directly measured inter-ionic distances were used.

a. Solid Solutions

To calculate the energy by the Wallace method the lattice parameters of the solid solutions must be known. Furthermore, use of this method leads to values of ΔH which are too high (see Table 7). We therefore calculated[34] the energy of mixing with an allowance for the electrostatic interaction after Tobolsky, Eqn. (3), and for the London forces after Lumsden, Eqn. (17). Comparison of values of Q thus calculated with the experimental values (see Table 1) shows very good agreement. For six binary systems marked with asterisks there are only the heats of mixing of the liquid phases. The values of Q in five of these are close to those calculated for the solid solutions. An exception is the $PbBr_2$–$PbCl_2$ system, for which even the signs of the thermal effect are different. As Delimarskii and Markov show[6], this system is a rare exception among solid solutions. They explain[6] the negative departures observed here by the formation of the compound PbClBr.

b. Fused Alkali Metal Halides and Nitrates

Unfortunately, heats of mixing of liquid solutions of alkali halides have not been studied calorimetrically; electrometric data are quite scanty. For comparison there are limited results obtained from the fusion diagrams[35] and from vapour pressures[25,39].

Table 2 contains the values of the contributions of the individual effects to the energy of mixing of salts with a common anion, calculated from Eqns. (4), (7), (17), and (19). The quantities Q found by Lumsden ($K_P + K_L$) do not agree very well with the experimental values. The Förland formula (4) gives a large deviation.

For salts with a common cation the main contribution to Q comes from the coulombic interaction, which decreases the energy of the system, and the dispersion interaction, which increases the potential of the solution. As Table 3 shows, these contributions are approximately the same and compensate one another. As a result the solutions are characterised by small departures from ideality ($\Delta H \simeq 0$). The results of the calculations are close to the available experimental data (see Table 3).

In solutions of salts with a common anion considerable negative departures are observed (see Table 2), connected mainly with the polarisation effect. On the other hand, the role of this effect is small for salts with a common cation.

Precision calorimetric investigations of the thermal effects of mixing of molten nitrates, made at 345–450°C by Kleppa[26] are of special interest for testing the various methods of calculation. Heats calculated with allowance for coulombic (4), non-polar (17), and polarisation (19) effects, and also found by Eqn. (5) are compared with experimental data in Table 4. The best agreement with experiment is obtained if we are restricted only to the polarisation effect. Somewhat worse results are given by the sum of all three constituents (coulombic, London, and polarisation). Eqn. (5) gives approximately the same deviations.

It is unfortunately difficult to solve the problem of the nature of the energy of mixing in molten nitrates, since even allowance for only the coulombic interaction between the nearest cations (5) gives approximately the same thermal effect as the polarisation of anions (ΔH_P).

c. Solutions of Alkali Metal Nitrates and Bromides with Silver and Thallium Salts

In solutions of $AgNO_3$ with alkali metal nitrates (MNO_3) it is observed[27] that there is a gradual change from positive departures (melts with $LiNO_3$ and $NaNO_3$) to negative

† Presumably the author means that the overestimate of the contribution of polarisation is supported only when a two-dimensional model is applied to the (three-dimensional) system (Ed. of Translation).

(KNO_3, $RbNO_3$). Here, as in AgBr–MBr melts [14], the increase in the radius of the M^+ cation leads to an increase in the negative departures from Raoult's law. An analogous dependence was found [27] in $TlNO_3$–MNO_3 melts.

Kleppa and Hersh [27] connect these phenomena with the fact that the lattices of the silver and thallium salts are only partly ionic. The non-coulombic contribution to the lattice energy is thought by them to be ~ 25 kcal for $AgNO_3$ and 15 kcal for $TlNO_3$.

The small changes in volume and energy (entropy) during fusion [40–45] are due to the asymmetric distribution of the electron density around the Ag^+ nucleus. Such a picture also holds true for SiO_2, where the bond between the silicon and the oxygen is very strong and the heat of fusion is small [46].

Förland thinks [40] that the change in energy during mixing is here due to the difference in structure of AgBr and MBr melts. Therefore during mixing one of the compounds or both changes its structure, which promotes an increase in energy. On the other hand, the energy of the solution should decrease, since the Ag^+ polarises Br^- more strongly than the alkali metal cations. Evidence of this is given by the lattice energy of AgBr being greater than that of MBr [47,48]. The absorption of heat during the mixing of AgBr with LiBr and NaBr is due mainly to the structural effects, and the liberation of heat in melts of AgBr with KBr and RbBr is mainly determined by the change in polarisation. It must also be taken into consideration that the tendency of silver salts to complex formation is evidence of the considerable relative significance of the directed bonds.

According to Markov and Delimarskii [6], here the complex-former is usually itself associated. When it passes into the solution, energy is expended in destroying these associates and is liberated as a result of the formation of new complexes with the second component.

The relative influence of these opposing effects is determined in an equimolecular solution of AgBr and MBr by the electrostatic field of the M^+ cation. With strong cations (Li^+) the breakdown of the associate predominates and heat is absorbed. The amount of the latter is determined to a first approximation by the quantity:

$$\delta = \frac{d_{Ag^+} - d_{M^+}}{d_{Ag^+} + d_{M^+}} \qquad (20)$$

On the other hand, with a weak partner (Rb^+) complex formation mainly occurs. The degree to which it takes place also depends on ratio (20), but with the opposite sign.

What has been stated allows the contribution of the directed bonds to the heat of mixing to be represented by the relation:

$$K_c = \Delta U \cdot \left(\frac{d_{M^+} - d_{Ag^+}}{d_{M^+} + d_{Ag^+}}\right) \qquad (21)$$

In this ΔU is the energy due to the existence of directed bonds in the complex-forming salt.

Hence the heat of mixing of salt melts containing strongly polarisable ions has contributions from at least four effects: coulombic, polarisation, intermolecular, and that due to complex formation and the breakdown of the initial associates.

Table 5 compares the heats of mixing calculated by the formula:

$$Q = K_P + K_L + K_e' + K_c \qquad (22)$$

with those found experimentally [14,27] and also with those calculated by the formula (6). The values of ΔU for nitrates (Ag^+ and Tl^+) were taken as -21 and -16 kcal.[27] As for bromides, we found the quantity $\Delta U \simeq -33$ kcal from the difference between the experimental and calculated values of the lattice energy. As Table 5 shows, formula (6) and Eqn. (22) allow the thermal effects of mixing to be evaluated with known accuracy.

d. Energy of Mixing of Halides with Cations of Different Valency

In recent years there have been studies [15,49–62] of the properties of solutions formed by molten $PbCl_2$, $CdCl_2$, $ZnCl_2$, $MgCl_2$, and alkali metal chlorides MCl, and also $PbBr_2$ and $CdBr_2$ with MBr. Some of these results are given in Table 8.

$PbCl_2$–LiCl solutions show small positive departures from Raoult's law. In $PbCl_2$–NaCl melts there are moderate negative departures which increase considerably on going to solutions with KCl or RbCl. The latter are due to the formation of complex ions, as is confirmed by the investigation of electrical conductivity [64–66], surface tension [67,68], viscosity [69], transport number [70,71], and specific and molar volumes [72].

The same regularity is observed in solutions of $CdCl_2$ and $ZnCl_2$ with MCl as in $PbCl_2$ melts.

On going from chloride solutions to the corresponding solutions of bromides there is an increase in the negative departures.

The relationships quoted earlier for evaluating the energy of mixing were developed for solutions of uni-univalent salts, having, for example, a common anion. For melts containing cations of different valency, Eqns. (3), (4), (15), (17) and (19) are inapplicable.

TABLE 8. Heats of mixing of halides in equimolar amounts with cations of different valencies.

System	Heat of mixing, kcal mole^{-1} calculated by the formulae: (23)	(5) $\Delta H = -140 \cdot \delta_1^2$	(24) $\Delta H = -15 \cdot \delta_1$	experimental	Reference
$PbCl_2$–LiCl	−0 65	−0.04	−0.24	+0.05	49
				+0.10	50
$PbCl_2$–NaCl	−1.05	−0.43	−0.84	−0.25	50
				−0.75	49
$PbCl_2$–KCl	−2.48	−1.65	−1.60	−1.25	49
				−1.50	50
$PbCl_2$–RbCl	−2.7	−2.2	−1.9	−1.4	50
				−2.2	49
$PbBr_2$–LiBr	−0.9	−0.05	−0.2		
$PbBr_2$–NaBr	−1.74	−0.4	−0.8	−0.5	50
				−1.0	63
$PbBr_2$–KBr	−2.8	−1.5	−1.5	−3.0	50
				−2.5	63
$PbBr_2$–RbBr	−3.45	−2.0	−1.8		
$CdCl_2$–LiCl	−2.0	−0.25	−0.64		
$CdCl_2$–NaCl	−3.1	−1.0	−1.2	−0.8	51
				−0.9	53
$CdCl_2$–KCl	−4.6	−2.65	−2.1	−2.5	51
$CdCl_2$–RbCl	−5.0	−3.2	−2.35		
$CdBr_2$–LiBr	−2.15	−0.22	−0.6		
$CdBr_2$–NaBr	−3.3	−0.9	−1.2	−0.25	52
$CdBr_2$–KBr	−4.6	−2.4	−1.9	−3.25	52
$CdBr_2$–RbBr	−8.4	−3.1	−2.2		
$ZnCl_2$–LiCl	−3.7	−0.42	−0.9		
$ZnCl_2$–NaCl	−5.4	−1.6	−1.6	−2.3	53
$ZnCl_2$–KCl	−7.3	−3.6	−2.5	−3.0	53
$ZnCl_2$–RbCl	−7.8	−4.4	−2.7	−4.6	53
$MgCl_2$–LiCl	−4.4	−0.65	−1.0	+0.1	15
$MgCl_2$–NaCl	−6.3	−1.7	−1.7	−1.5	15
$MgCl_2$–KCl	−8.2	−4.1	−2.5	−4.0	15
$MgCl_2$–RbCl	−8.8	−4.7	−2.9	−6.0	15

When allowance is made for the difference in the charges of the cations in the derivation of the expression for the contribution from the change in polarisation Eqn. (19) becomes, to a first approximation:

$$K'_P = -1060 \cdot N \cdot \alpha \cdot \left[\frac{2}{(r^{2+})^3} - \frac{1}{(r^+)^3}\right]^2. \quad (23)$$

The energy of mixing found by this formula truly gives the change in Q in AX_2–BX melts. An increase in the radius of the M^+ ion increases the negative departures, whereas an increase in the dimensions of M^{2+} decreases it. The negative departures in bromides under conditions otherwise equal are stronger than in chlorides, since the polarisability of Br is greater than that of Cl. However, the size of the calculated heats of mixing is much higher (see Table 8) than that found experimentally. As the heat of mixing is determined now not by the difference $(r_1 - r_2)$ but by the relation $(\frac{1}{2}r^{2+} - r^+)$, then Eqn. (5) can be used as an empirical formula:

$$\Delta H = -U \cdot \delta_1^2 \quad (24)$$

in which:

$$\delta_1 = \frac{\frac{r^{2+}}{2} - r^+}{d_1 + d_2}$$

Unlike formula (5), it is not based on any physical model of the solution. The quantity U essentially should be close to the arithmetic mean of the lattice energies of the salts. The closest results to experiment are obtained (see Table 8) on taking U = -140 kcal, which is much less than $\frac{1}{2}(U_{AX_2} + U_{BX})$.

An equation analogous to (21) in which the ratio $\delta = \frac{d_1 - d_2}{d_1 + d_2}$ is used instead of $\delta_1 = \frac{\frac{r_1}{2} - r_2}{d_1 + d_2}$ is less convenient. The expression

$$\Delta H = -15 \cdot \delta_1 \quad (25)$$

also, like formulae (23) and (24), does not give (see Table 8) the change in sign of the departures of the solutions from the ideal.

Table 9 gives the experimental results on the thermochemistry of solutions of alkali metal nitrates [27] and carbonates [62] with the corresponding calcium salts. The use of empirical equations (24) and (25) gives somewhat better results than the more well-founded formula (23).

Expressions (22), (5), and (6) poorly describe the experimental results for solutions of the alkaline earth metals (see Table 10). This cannot be said about the chlorides and bromides of other metals.

TABLE 9. Heats of mixing of molten alkali metal nitrates and carbonates with calcium salts (for equimolar compositions).

System	Heat of mixing, kcal mole^{-1} calculated by the formulae: (23) K'_P	(24) $-225 \cdot \delta_1^2$	(21) $-20 \cdot \delta_1$	experimental	Reference
$Ca(NO_3)_2$–$LiNO_3$	−0.6	−0.3	−0.74	+0.4	27
$Ca(NO_3)_2$–$NaNO_3$	−1.1	−1.2	−1.5	−1.1	27
$Ca(NO_3)_2$–KNO_3	−1.4	−3.2	−2.4	−3.0	27
$Ca(NO_3)_2$–$RbNO_3$	−1.8	−4.2	−2.8	−4.35	27
$CaCO_3$–Li_2CO_3	−0.8	−0.3	−0.75	−0.6	73
$CaCO_3$–Na_2CO_3	−1.47	−1.23	−1.50	−1.4	73
$CaCO_3$–K_2CO_3	−2.0	−3.2	−2.5	−2.9	73
$CaCO_3$–Rb_2CO_3	−2.6	−4.3	−2.9		

TABLE 10. Heats of mixing in molten chlorides and bromides of bivalent metals (for equimolar compositions).

Melts	Heat of mixing, kcal mole^{-1} found by the formulae: (22)	(5) $-600 \cdot \delta^2$	(6) $-80 \cdot \delta$	experimental	Reference
$PbCl_2$–$CaCl_2$	+1.3	−1.2	+1.1	+1.8	50
$PbCl_2$–$SrCl_2$	+0.9	−0.4	+0.8	+0.1	50
$PbCl_2$–$BaCl_2$	−0.7	−0.1	−0.8	−0.4	50
$CdCl_2$–$CaCl_2$	0	0	0		
$CdCl_2$–$SrCl_2$	−0.3	−0.35	−0.35		
$CdCl_2$–$BaCl_2$	−1.7	−2.2	−2.2	−1.6	50
$ZnCl_2$–$CaCl_2$	−1.2	−1.0	−1.0		
$ZnCl_2$–$SrCl_2$	−2.5	−2.2	−2.2		
$ZnCl_2$–$BaCl_2$	−5.6	−5.8	−5.8	−4.5	53
$MgCl_2$–$CaCl_2$	−2.2	−1.0	−1.0		
$MgCl_2$–$SrCl_2$	−3.9	−3.3	−3.3		
$MgCl_2$–$BaCl_2$	−7.5	−6.9	−6.9		
$PbCl_2$–$CdCl_2$	−1.1	−1.4			
$PbCl_2$–$ZnCl_2$	−5.0	−4.3		−9.0	74
$PbCl_2$–$MgCl_2$	−5.7	−5.3			
$CdCl_2$–$ZnCl_2$	−1.1	−0.9			
$CdCl_2$–$MgCl_2$	−1.5	−1.3			
$ZnCl_2$–$MgCl_2$	~0	~0			
$PbBr_2$–$ZnBr_2$	−2.2	−3.8		+0.9	16
$PbCl_2$–$PbBr_2$	−0.2	−0.4		⩽0	17

It is also interesting to note that for oxides and silicates the comparison of calculated values of Q with the published information gives reasonable agreement in general (see Tables 11 and 12).

e. Melts of Reciprocal Salt Systems

Voskresenskaya [78-80] confirmed Kablukov's prediction that the stable pair of salts will be that which corresponds to the liberation of heat during the double decomposition in the solid state. The determination of the direction of the double decomposition from the thermal effects is permissible here, since the sign of ΔZ for the reaction usually changes at temperatures higher than the liquidus. A recommendation has been made [78] for the calculation of the heat of reaction by the lattice energies (U) of the individual salts, found by Kapustinskii's formula:

$$U = 256 \cdot \frac{n \cdot z_1 \cdot z_2}{r_1 + r_2}, \quad (26)$$

where z_1 and z_2 are the charges of the ions.

TABLE 11. Energy of mixing of molten oxides.

Melts	Constituent energies of mixing, calculated by the formulae: (19) K_P	(17) K_L	(7), K_e	Energy of mixing $Q=-800 \cdot \delta^2$	$Q=K_P+K_L+K_e$	Q_{exp}	reference
FeO–MnO	−0.08			−0.04	−0.08		
FeO–CaO	−2.0		−0.2	−2.4	−2.2	−6.8	22
FeO–MgO	0	0.15		0	+0.15		
FeO–NiO	−0.07			−0.16	−0.07		
FeO–CoO	0			0	0		
FeO–ZnO	−0.08			−0.05	−0.08	0	23
FeO–PbO	−6.5	0.20	−0.9	−8.0	−7.2		
FeO–BaO	−7.6		−0.9	−11.5	−8.5		
MnO–CaO	−1.3		−0.2	−1.8	−1.5		
MnO–MgO	−0.1	0.20		−0.1	+0.1		
MnO–NiO	−0.3			−0.3	−0.3	>0	24,75
MnO–CoO	−0.1			−0.1	−0.1		
MnO–ZnO	0			0	0		
MnO–PbO	−4.9	0.15	−0.6	−8.0	−5.4		
MnO–BaO	−6.1		−0.8	−10.0	−6.9		
CaO–MgO	−2.1		−0.2	−2.8	−2.3		
CaO–NiO	−2.8		−0.2	−2.9	−3.0		
CaO–ZnO	−1.3		−0.2	−2.0	−1.5		
CaO–PbO	−1.2	0.2	−0.2	−2.3	−1.2		
CaO–BaO	−1.8		−0.2	−3.9	−2.0		
MgO–NiO	−0.1		−0.1	−0.1	−0.2	~0	24,75
MgO–ZnO	−0.1			−0.1	−0.1		
MgO–PbO	−6.4	0.6	−0.8	−9.6	−6.6		

TABLE 12. Energy of mixing of certain molten silicate solutions.

Melts	Constituent energies of mixing		Energy of mixing found by the formulae:			Reference
	K_P' (Lumsden) (23)	K_e'' (Förland)	$Q=K_P'+K_e''$	$Q=-4\cdot\delta_1^2$	expt.	
FeO—SiO_2	—10.2	—0.7	—10.9	—13.3	—10.0	76
CaO—SiO_2	—20.3	—1.3	—21.6	—28.8	—27.0	77
MnO—SiO_2	—11.5	—0.9	—12.4	—14.0	—10.0	77
MgO—SiO_2	—9.6	—0.8	—10.4	—12.6	—27.0	77
PbO—SiO_2	—30.4	—2.1	—32.5	—48.5		
ZnO—SiO_2	—11.6	—0.9	—12.6	—14.0	—14.3	76
Na_2O—SiO_2	—17.7	—1.2	—18.9	—24.0		

As our calculations showed, the best agreement is obtained by using the lattice energies found experimentally.

Comparison of the thermal effects of the double decompositions ΔH_R with the heats of mixing of the solutions ΔH with a common ion shows that the former are appreciably greater than the latter. Thus, for LiF–CsF melts the quantity ΔH is 5 kcal, but the heats ΔH_R for the reciprocal systems LiCl + CsF, LiBr + CsF, and LiI + CsF are respectively -9, -13, -15 kcal per mole solution.

To a first approximation the energy of mixing Q of the reciprocal system AX + BY = AY + BX is equal to the sum of those for four systems with a common ion: AX + BX, AY + BY, AX + AY, and BX + BY. Thus Q_R for the system LiI + CsF = LiF + CsI is 15.5 kcal, and the sum of quantities Q for the solutions LiF + CsF, LiF + LiI, LiI + + CsI, and CsF + CsI is 14.8 kcal.

In reactions with ions of different valency the energies of mixing are greater. The differences between the quantities calculated by the Kapustinskii formula and those found experimentally are more significant. As has been shown[78], the experimental values are usually much less than those calculated.

The great difference between calculation and experiment is partly connected with the increase in the fraction of directed bonds in salts of higher valency. It therefore seems desirable to use data on heats of formation. However, there still remains an indeterminacy, connected with the departure of the heat capacity of the components from the Kopp–Neumann law.

It is interesting to note that here also there is a link between the quantities ΔH_R for reciprocal systems and the values of ΔH for their consistuent solutions with a common ion.

All the above shows that the calculation of the energy of mixing from the properties of the individual particles is still in its earliest stages even for such simple systems as ionic melts. We thought it desirable to review these publications in order to draw the attention of investigators to future developments in this important problem.

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REARRANGEMENTS INVOLVING THE CLEAVAGE OF N–N OR N–O BONDS AND FORMATION OF A NITRILE GROUP

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1. INTRODUCTION

There has been much recent work on rearrangements in which an N–N or N–O bond is broken and a nitrile group formed.

Compounds which can undergo this conversion include substituted aldehyde hydrazones, their cyclic analogues, the 3-unsubstituted pyrazolines and indazoles, and their cyclic and acyclic oxygen analogues, that is, aldoximes and 3-unsubstituted isoxazoles.

The nitrile fission of N–N or N–O bonds is observed under diverse experimental conditions: by the action of salts of complex-forming metals or platinum group metals; in the pyrolysis of hydrochlorides or quaternary salts; in the Hofmann degradation of quaternary ammonium bases; and by the action of nucleophilic reagents. The lack of data on the mechanism of the reaction and the variety of conditions, despite the external similarity of the processes, often hinder their comparison and generalisation.

2. NITRILE FISSION OF N–N OR N–O BONDS BY ELECTROPHILIC REAGENTS OR METAL CATALYSTS†

In 1910 Arbuzov observed[1,2] that heating aliphatic aldehyde phenylhydrazones to 180–200° with catalytic

† Metal catalysts are only formally included in this section, in view of the lack of knowledge of the mechanism of their action and the paucity of experimental material.

amounts of Cu_2Cl_2, $PtCl_2$, or $ZnCl_2$ produces the corresponding nitrile and aniline:

$$R{-}CH{=}N{-}NHC_6H_5 \xrightarrow[t^\circ]{Cu_2Cl_2} R{-}C{\equiv}N + H_2N{-}C_6H_5,$$

that is, fission of the aldehyde phenylhydrazone occurs instead of the normal Fischer indole synthesis. The phenylhydrazones of lower aliphatic aldehydes produce mainly the corresponding indoles, but those of higher aldehydes undergo mainly the nitrile fission.

Somewhat earlier a similar fission was observed by Anselmino [3] in the dry distillation of salicylaldehyde phenylhydrazone, which produces salicylonitrile and aniline together with benzene and ammonia.

In 1921 Maihle [4,5] observed nitrile fission when attempting catalytic hydrogenation of various aliphatic aldehyde phenylhydrazones at 180–190° over nickel.

It has recently been shown [6] that aromatic aldehyde phenylhydrazones also rearrange into amine and nitrile under Arbuzov conditions (Cu_2Cl_2, 220°); this is an exothermic reaction. The reaction is in fact general for compounds R–CH=N–NR′R″; thus diphenylamine and the corresponding nitrile are obtained from benzaldehyde phenylhydrazone (R = R′ = R″ = C_6H_5) and the phenylhydrazones of propionaldehyde and isovaleraldehyde (R = = alkyl, R′ = R″ = C_6H_5). Benzaldehyde benzoylhydrazone, which with phosphoryl(V) chloride under milder conditions disproportionates to benzaldehyde azine and 2,5-diphenyl--1,3,4-oxadiazole [7,8], also undergoes the nitrile rearrangement when heated with copper(I) chloride, yielding benzamide and benzonitrile:

$$C_6H_5CONH{-}N{=}CHC_6H_5 \xrightarrow[t^\circ]{Cu_2Cl_2} C_6H_5CONH_2 + N{\equiv}C{-}C_6H_5.$$

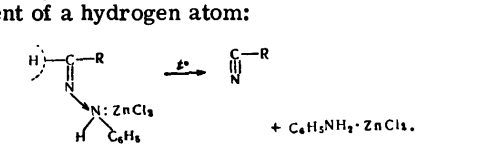
There is only a slight tendency for dialkylhydrazones to decompose with fission of the N–N bond [6]. For example, the decomposition of benzaldehyde dimethylhydrazone (R = C_6H_5, R′ = R″ = CH_3) under Arbuzov conditions (Cu_2Cl_2, 230°) produces benzonitrile in no more than 18% yield, and this falls to 11% if the copper(I) chloride is replaced by anhydrous zinc chloride. Heating heptanol diethylhydrazone at 260° for 4 h in the presence of copper(I) chloride gives only 6% of heptanenitrile and 9% of diethylamine; most of the hydrazone is recovered unchanged [9].

It has not proved possible to obtain an amine and nitrile from aldehyde monoalkylhydrazones, because of their decomposition with evolution of nitrogen [6]; thus when benzaldehyde isopropylhydrazone is heated with copper(I) chloride the double bond is probably displaced and the resulting azo-compound then decomposes, isobutylbenzene and stilbene being obtained:

$$(CH_3)_2CH{-}NH{-}N{=}CHC_6H_5 \longrightarrow (CH_3)_2CH{-}N{=}N{-}CH_2C_6H_5 \longrightarrow$$
$$\longrightarrow (CH_3)_2CH\cdot + N_2 + \cdot CH_2C_6H_5 \longrightarrow (CH_3)_2CHCH_2C_6H_5.$$

The conversion of ketone benzylhydrazones proceeds similarly, but in more complex fashion [10].

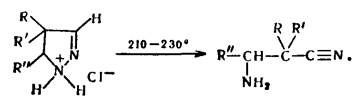
In the fission of aldehyde phenylhydrazones the catalyst ($ZnCl_2$, Cu_2Cl_2, $PtCl_2$) apparently first attaches itself to the more basic nitrogen atom, causing a redistribution of electron density and then cleavage of the N–N bond and displacement of a hydrogen atom:



The amine is often obtained in higher yield than the nitrile, probably because of the formation of the intermediate zwitter-ion $R{-}\overset{-}{C}{=}\overset{+}{N}$, which can polymerise. This, and the influence of the solvent on the reaction when copper(I) chloride is used, indicate that the reaction occurs with heterolytic cleavage of the N–N bond. Benzaldehyde phenylhydrazone produces benzonitrile by the action of copper(I) chloride in very much greater yield in polar solvents than in non-polar; in protic (for example, diethyleneglycol) and aprotic polar solvents (for example, dibutyl phthalate, benzyl benzoate, or diphenyl oxide) the yield is about the same (50–60%), but in non-polar solvents such as 2-methylnaphthalene or liquid paraffin the benzonitrile is obtained in ~ 10% yield [11].

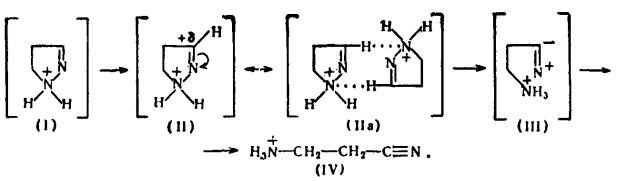
The analogous fission of the N–N bond with formation of a nitrile group is also known in the cyclic analogues of aldehyde hydrazones, the pyrazolines.

In 1962 Grandberg and Potapova found [12] that when heated to 230° 4-ethyl-5-propylpyrazolinium chloride decomposes to yield 3-amino-2-ethylhexanenitrile. This reaction has also been observed [13] with a number of other pyrazolines containing a hydrogen atom in position 3:.



Protonation of the 1-nitrogen atom therefore produces the same rearrangement, with cleavage of the N–N bond, as complex-formation with copper(I) chloride in Arbuzov's experiments. The reaction is highly exothermic, and with large amounts of material can get out of control.

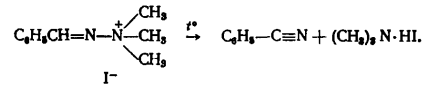
The pyrazolinium cation (I) formed by the acid is considered [13] to undergo a redistribution of electron density:



Because of the positive charge on the 1-nitrogen atom (for this is the salt-forming atom) [14], the electron pair forming the nitrogen–nitrogen σ bond is attracted towards the 1-nitrogen atom, and this causes a displacement of the electrons of the carbon–nitrogen double bond towards the nitrogen atom, leaving a residual positive charge on the 3-carbon atom; thus in the pre-rearrangement state, (II) or (IIa), the bond between the 3-carbon atom and the hydrogen atom is weakened, the the hydrogen is readily lost as a proton. The nitrogen–nitrogen bond is also weakened, because of the strong attraction of the electron pair towards the first nitrogen atom. In the rearrangement step the proton migrates from position 3 to the electron pair associated with the 1-nitrogen atom, and the nitrogen–nitrogen bond finally breaks to form the intermediate (III), which immediately rearranges to the β-aminonitrile cation (IV).

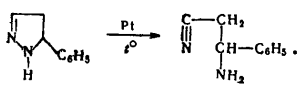
Under the very severe reaction conditions, the resulting β-aminonitriles partially lose ammonia to form αβ-unsaturated nitriles which polymerise during the reaction. These side-reactions greatly reduce the yield of β-aminonitrile, which does not exceed 25%. With 4,4-dimethyl--5-isopropylpyrazoline, where ammonia cannot be lost in this way, the yield reaches 36%.

A reaction similar to the nitrile fission of pyrazolinium chlorides is also possible with aldehyde dialkylhydrazones (when protonation or quaternation occurs on the farther nitrogen atom)[6]; thus pyrolysis of benzaldehyde dimethylhydrazonium chloride at 140° produces an exothermic reaction (the temperature rising to 230°) with the formation of benzonitrile (22%) and dimethylamine (48%), and pyrolysis of benzaldehyde dimethylhydrazone methiodide at 230° yields benzonitrile (21%) and trimethylamine (49%):

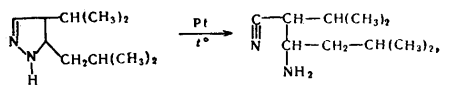


1,1-Dimethylpyrazolinium iodide also produces an aminonitrile when heated at 150° to 180° for a short time, but in low yield[15].

Colloidal platinum also causes rearrangement of 3-unsubstituted pyrazolines into aminonitriles[16]; thus heating 5-phenylpyrazoline to 140° with platinum black gave 3-amino-3-phenylpropanenitrile in 65% yield, instead of the expected mixture of pyrazole and pyrazolidine:



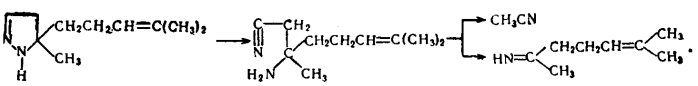
Similarly at 120–140° platinum produced 3-amino-2-isopropyl-6-methylhexanenitrile from 5-isobutyl-4-isopropylpyrazoline:



but the greater part of the material was converted into high-boiling condensation products. With 4-ethyl-5-propylpyrazoline the reaction is exothermic, with evolution of much ammonia, and the main reaction products are resinous materials, probably from polymerisation of the unsaturated nitrile formed.

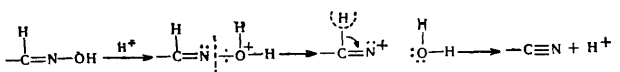
Attempts to carry out the rearrangement using a Raney nickel catalyst have been unsuccessful.

Kizhner has noted[17] that heating 5-isohexenyl-5-methylpyrazoline with platinised alkali gives acetonitrile and a methylheptenone imine in addition to the corresponding cyclopropane hydrocarbon. Apparently this anomalous reaction also passes through the β-aminonitrile stage, and under the severe reaction conditions this decomposes in the way that is known, for example, for Mannich bases[18]:

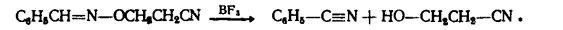


In addition to the substituted aldehyde hydrazones and pyrazolines, their oxygen analogues the aldoximes also produce nitriles under the action of acidic reagents.

Primarily this is a dehydration of aldoximes to nitriles by means of acids. The mechanism of the reaction is essentially analogous to that considered above for the nitrile fission of substituted aldehyde hydrazones and pyrazolinium chlorides, and may be represented[19]:



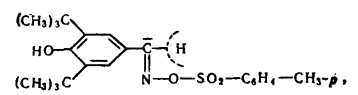
Unlike aldoximes themselves, their *O*-ethers are very stable; they are unaffected by aqueous or alcoholic hydrogen chloride or bromide or by 60% sulphuric acid[20], and like ketoxime *O*-ethers they do not undergo the Beckmann rearrangement[21], which is explained by their inability to form salts[22,23]. However, in the presence of a complex-forming reagent such as boron trifluoride, which can form an oxonium fluoroborate, it has been possible to decompose benzaldehyde oxime *O*-2-cyanoethyl ether into benzonitrile and 2-cyanoethanol[24]:



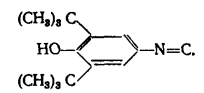
The addition products of aldoximes with methylketen diethyl acetal $CH_3CH_2C(OC_2H_5)_2-O-N=CH-R$ decompose to form $R-C\equiv N$ and $R-N=C$ when boiled in ether with boron trifluoride and mercury(II) oxide[25].

In the course of their comparison of the nitrile rearrangements of oximes and hydrazones, Grandberg and coworkers[6] obtained benzonitrile from benzaldehyde oxime *O*-benzyl ether under Arbuzov reaction conditions (210°, Cu_2Cl_2).

Müller and Narr[26] observed a new type of Beckmann rearrangement from aldoxime *p*-tolylsulphonates such as



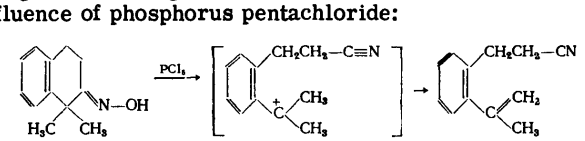
which when prepared in absolute alcohol at -30° gave *p*-toluenesulphonic acid and a 72% yield of the isonitrile



Depending on the mesomeric, inductive, and steric effects of the substituents on the benzene ring, the tolylsulphonates *syn*-Ar–CH=N–OT either ionise at the N–O bond with subsequent rearrangement, leading to formation of the isocyanide ArNC, or lose the proton from the CH-group, giving the nitrile ArCN, or undergo both conversions.

Many investigators have indicated the similarity of the nitrile rearrangements of substituted aldehyde hydrazones[6,16,27] and 3-unsubstituted pyrazolines[6,16] to the Beckmann rearrangement of the second type. This rearrangement is particularly characteristic of α-hydroxyketone oximes, monoximes of certain aliphatic-aromatic α-diketones, aromatic ketoximes containing a tertiary carbon atom in the α-position to the oxime group, and some oximes of cyclic ketones. Information on this rearrangement, which also involves cleavage of an N–O bond and formation of a nitrile, may be found in reviews[28,29].

Conley and Lange[30] recently demonstrated the intermediate formation of carbonium ions in this reaction, using the rearrangement of cyclic ketoximes under the influence of phosphorus pentachloride:

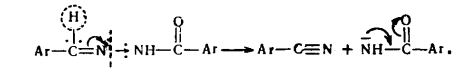


The carbon–carbon bond splits heterolytically, with formation of a carbanion at the carbon atom of the C=N double bond and a carbonium ion at the quaternary carbon atom, the latter being stabilised by elimination of a proton. The overall process is thus similar to a fragmentation reaction[31].

3. NITRILE REARRANGEMENTS PRODUCED BY NUCLEOPHILIC REAGENTS

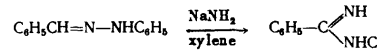
Naumov and coworkers[11] have established that substituted aldehyde hydrazones also decompose into nitrile and amine when heated to 260–290° with a catalytic amount of solid potassium hydroxide or sodium amide, thus benzaldehyde phenylhydrazone produces benzonitrile and aniline‡. Similarly benzaldehyde diphenyl-, acetyl-, and benzoyl-hydrazones decompose to give benzonitrile with diphenylamine, acetamide, and benzamide respectively. Fission produced by solid alkalis proceeds more smoothly than with copper(I) chloride, but yields are about the same.

The reaction apparently proceeds by β-elimination: the hydroxyl or amido-group attacks the "aldehydic" hydrogen atom, and the deprotonisation increases the polarisation of the nitrogen–nitrogen bond, which when heated splits anionically. The reaction is thus apparently heterolytic:



Nitrile fission produced by alkalis is not characteristic of aldehyde mono- or di-alkylhydrazones; as Todd[33] showed, monoalkylhydrazones decompose when heated with solid potassium hydroxide with evolution of nitrogen (as in the Kizhner reaction). On the other hand, benzaldehyde dimethyl- and diethyl-hydrazones are stable to solid alkalis[6,11,33].

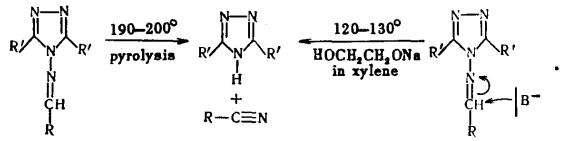
A particular conversion of aldehyde phenylhydrazones involving cleavage of the nitrogen–nitrogen bond is the Robev amidine rearrangement. In 1954 Robev found[34,35] that phenylhydrazones of aromatic aldehydes rearrange to amidines when heated to 140–145° with sodium amide in xylene:



Under the reaction conditions the amidine is partially decomposed into aniline and the nitrile, and this reaction goes to completion at a more elevated temperature[36]. Since aromatic amines and nitriles are known to produce *N*-phenylamidines by the action of sodium amide in xylene[37], the amidine rearrangement might have been thought to proceed by initial decomposition of the hydrazone into amine and nitrile followed by reaction between the latter[36,38]; however, it has recently been decisively established[39–43] that the reaction involves homolytic cleavage of the N–N bond, and is not a nitrile fission of the type under review.

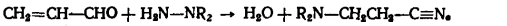
Hodgkins and King[44] observed the formation of benzonitrile in the photochemical decomposition of benzaldehyde azine in the presence of benzophenone, and thought it to involve a radical mechanism, the intermediate azine being reduced to benzaldehyde phenylhydrazone which then undergoes the nitrile fission.

Becker and Timpe have recently found[45] that the azomethines formed from aromatic or heterocyclic aldehydes and 4-amino-1,2,4-triazole decompose into 1,2,4-triazole and the corresponding nitrile when heated to 190–200°. Kinetic studies showed the reaction to be catalysed by bases, and in accordance with this the decomposition temperature in the presence of a base ($HOCH_2CH_2ONa$) is somewhat lower (120–130°) than in pure pyrolysis:

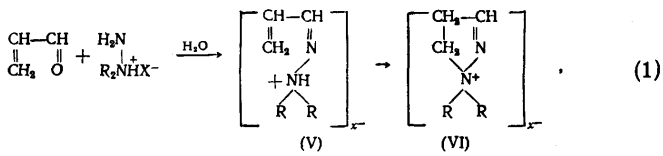


This was proposed as a preparative reaction for various nitriles (other than-aliphatic§), giving yields of up to 85%.

In 1960 Ioffe and Zelenin found[46] that the condensation of acrolein with unsymmetrical dimethyl- or diethyl-hydrazine in the cold in a weakly acid medium gives not the expected unsaturated *NN*-dialkylhydrazones, but β-dialkylaminopropionitriles:

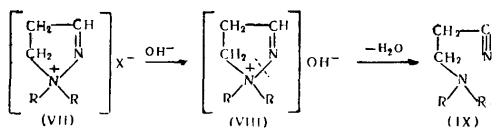


Under the same conditions αβ-unsaturated ketones produce only the stable dialkylhydrazones[47]. In 1962 these workers showed[15,38,48–50] that their formation of β-dialkylaminopropionitriles proceeds by cyclisation of the acrolein and unsymmetrical dialkylhydrazine to produce a pyrazolinium salt:



(1)

followed by decomposition of the quaternary pyrazolinium base (by addition of alkali at room temperature):

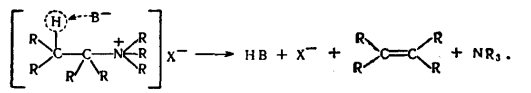


(2)

The structure of the quaternary pyrazolinium salt (VII; R = CH_3) was proved by cross-synthesis from methylhydrazine and acrolein. Addition of 50% NaOH to a concentrated aqueous solution of 1,1-dimethylpyrazolinium iodide causes immediate separation of β-dimethylaminopropionitrile, scheme (2) with R = CH_3, X = I. Several other 1-methylpyrazolinium iodides substituted in positions 1, 4, and 5 decompose analogously[38].

Ioffe and Zelenin concluded that the aminonitrile rearrangement of quaternary pyrazolinium salts proceeds analogously to the Hofmann degradation of quaternary ammonium bases.

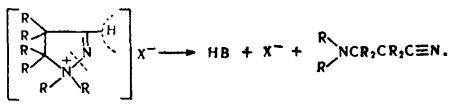
The structural feature characteristic of compounds which undergo this type of rearrangement is the presence of a quaternary nitrogen atom and a hydrogen atom in position 3, that is, in the β-position relative to the quaternary atom. Quaternary ammonium compounds are known to decompose under the action of bases:



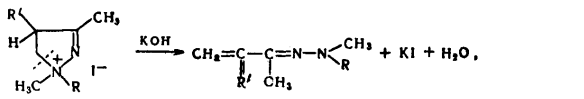
‡ Wolf[32] heated benzaldehyde phenylhydrazone with alcoholic sodium ethoxide at 165° for 20 h and obtained aniline (57%) and benzoic acid (89%). Benzonitrile may have been produced initially.

§ Aliphatic aldehydes give alkylidenebisamines with 4-amino-1,2,4-triazole, and not azomethine derivatives[45].

With quaternary pyrazolinium salts there is an initial abstraction of the proton at the C=N double bond produced by the action of the base (alkali), and then formation of the C≡N bond:

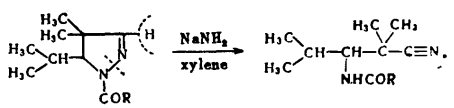


3-Substituted quaternary pyrazolinium salts, for which the aminonitrile rearrangement is impossible, invariably decompose by opening of the ring at the nitrogen–carbon bond, with formation of unsaturated *NN*-dialkylhydrazones[51]:

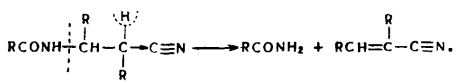


where (R = CH_3 or C_2H_5; R′ = H or CH_3). The reaction is carried out by heating with the solid potassium hydroxide to 130–160°, that is, to a considerably high temperature than is required by the aminonitrile rearrangement. However, these conditions are the same as for the Hofmann degradation of other hydrogenated nitrogen-containing heterocyclic compounds (pyrrolidine, piperidine, etc.)[52,53].

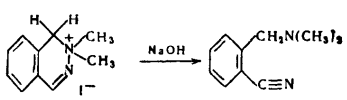
Naumov and coworkers have found[11] that 3-unsubstituted 1-acyl- (including 1-benzoyl- and 1-benzenesulphonyl-) pyrazolines can also produce the corresponding acylaminonitriles when heated with sodium amide in xylene:



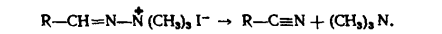
If position 4 of the pyrazoline ring carries a hydrogen atom a further degradation becomes possible:



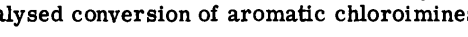
In 1962 Smith and Otremba observed[54] that 2,2-dimethyl-1,2-dihydrophthalazinium iodide is converted into *o*-dimethylaminomethylbenzonitrile by treatment with an aqueous solution of sodium hydroxide:



On the assumption that this is a general reaction for *NNN*-trimethylhydrazinium salts obtained from aldehydes, Smith and Walker studied it in some detail[55], and showed that the quaternary salts derived from the dimethylhydrazones of various aldehydes (aliphatic, aromatic, and unsaturated) are smoothly converted into the corresponding nitriles by treatment with a methanol solution of sodium methoxide



Smith considered his reaction to have an affinity with the base-catalysed conversion of aromatic chloroimines into nitriles:



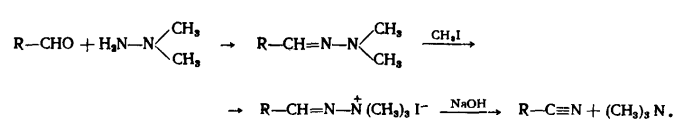
described in 1930 by Hauser and Gillaspie[56], that is, β-elimination occurs, and it differs from the chloroimine reaction only in the group which is eliminated.

Smith and Walker studied the behaviour of quaternary aldehyde hydrazonium salts in aqueous solution. The salts derived from aromatic aldehydes with electron-accepting substituents underwent slow β-elimination when the solutions were boiled for 6–8 h; the trimethylhydrazonium iodides obtained from *o*-nitro-, *m*-nitro-, and *o*-chlorobenzaldehyde gave the corresponding nitriles in yields of 75, 45, and 82% respectively. On the other hand, analogous treatment of benzaldehyde derivatives led to a recovery of 47% of the starting material, together with a mixture of benzaldehyde and benzonitrile. The quaternary *p*-dimethylaminobenzaldehyde hydrazonium iodide also underwent simultaneous elimination and hydrolysis when boiled in aqueous solution. Treatment of benzaldehyde derivatives with 1 *N* NaOH at room temperature caused rapid separation of an oil, which was also a mixture of benzonitrile and benzaldehyde.

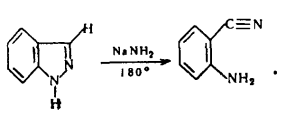
Hauser and coworkers[57] showed the conversion of aromatic chloroimines to nitriles to be of the second order kinetically.

Smith and Walker consider that the elimination reaction shown by the quaternary hydrazonium salts in water alone also proceeds by an E_2 mechanism, the water acting as the base. Under these conditions the elimination can be considered as proceeding by a mechanism similar to that of the decomposition of the trimethyl-2-(*p*-nitrophenyl)-ethylammonium ion to *p*-nitrostyrene in aqueous solution[58]; here electron-withdrawing substituents increase the acidity of the β-hydrogen atom and so facilitate the elimination. With the quaternary hydrazonium salts obtained from unsubstituted benzaldehyde or *p*-dimethylaminobenzaldehyde, the reduced acidity of the β-hydrogen atom enables hydrolysis to complete successfully with the β-elimination reaction. Smith and Walker find these results to be in accordance with those of Hauser and coworkers[57], who obtained relative rates of reaction of 1 : 7.7 : 540 for the sodium hydroxide-catalysed decomposition of chloroimines derived from benzaldehyde, *o*-chlorobenzaldehyde, and *o*-nitrobenzaldehyde.

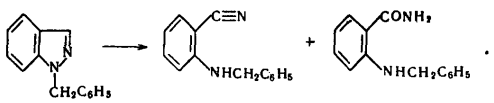
The alkaline fission of quaternary aldehyde hydrazonium salts was described almost simultaneously by other workers also[6,59–61]. It has also been proposed to use this reaction for the preparation of nitriles from aldehydes in yields of 40–80%[59]



Huisgen and coworkers observed[62] the formation of *o*-aminobenzonitrile when indazole is heated to 180° with sodium amide:

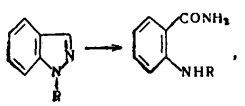


When attempting the amination of certain indazoles with alkali metal amides, Simonov and coworkers found[63] that the action of sodium amide and sodium hydroxide on 1-benzylindazole in xylene causes expansion of the pyrazole ring to a pyrimidine ring, and also ring opening with formation of the amide and nitrile of *N*-benzylanthranilic acid:



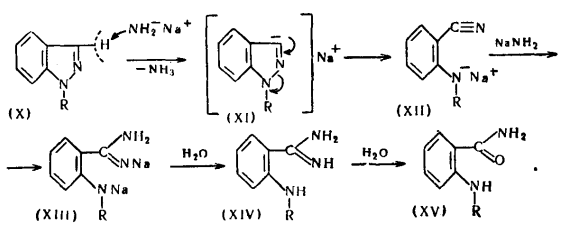
The same result is obtained in a current of ammonia and when thoroughly dry air is passed through the reaction mixture. 1-Benzylindazole reacts very readily with potassium amide in liquid ammonia[65], the main product being the nitrile of *N*-benzylanthranilic acid (67% yield).

The pyrazole ring is also opened when 1-alkylindazoles are heated with sodium amide in xylene in the presence of sodium hydroxide, with the formation of amides of *N*-alkylanthranilic acids in 40–50% yields[66]:



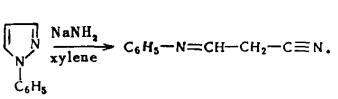
where R = CH_3, C_2H_5, n-C_3H_7 or iso-C_3H_7. Under the same conditions 1-butylindazole yields the nitrile of *N*-butylanthranilic acid in addition to the amide.

The ring is also opened when 1-arylindazoles react with sodium amide in xylene, producing nitriles, amides, or amidines of *N*-phenylanthranilic acid, depending on the structure of the aryl moiety[65]. Apparently[65] there is first a direct nucleophilic attack by the sodium or potassium amide on the hydrogen in position 3 of the pyrazole ring (X) (3-substituted indazoles do not react with sodium amide) with abstraction of a proton, liberation of ammonia and formation of the unstable sodium derivative (XI). After this, or at the same time, there is a redistribution of electron density around the ring, leading to weakening and then cleavage of the N–N bond with formation of the nitrile (XII):

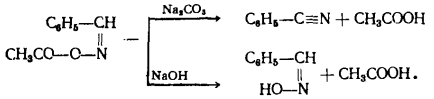


The nitrile (XII) adds on sodium amide at the nitrile group to give the sodium salt of the corresponding amidine (XIII) which, when water is added to the reaction mixture after the reaction, is readily hydrolysed to the amide of the corresponding *N*-substituted anthranilic acid (XV).

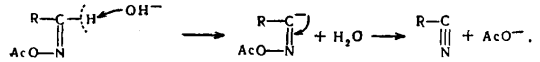
Recently Bobrova achieved the opening of the pyrazole ring itself[67]; when 1-phenylpyrazole and certain other 3-unsubstituted pyrazoles are heated with sodium amide in xylene the N–N bond opens to form the corresponding β-iminonitriles:



Aldoximes and their derivatives can also undergo nitrile fission of the N–O bond by the action of alkaline substances. Hantsch showed[68] that in addition to alkaline hydrolysis, acetyl β-benzaldehyde oxime can undergo fission of the N–O bond under the action of sodium carbonate in the cold:

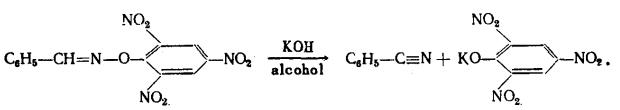


Benger and Brady.[69] studied this reaction with many acetylated aromatic β-aldoximes and showed that the nitrile may be formed as follows:



They consider that the deprotonisation under the action of the nucleophilic reagent leads to a redistribution of electron density and rupture of the N–O bond.

Unlike the acetylated oximes, the alkyl *O*-ethers are very stable, and even withstand boiling with 2 *N* NaOH.[20] However, benzaldehyde oxime *O*-2,4-dinitrophenyl ether[70] and benzaldehyde oxime *O*-2,4,6-trinitrophenyl ether[71] decompose to produce benzonitrile when boiled with alcoholic alkali:



In the 1930's it was suggested independently by several workers that when a molecule HX (where X is halogen, acetoxy, etc.) is split off from certain organic compounds by the action of bases a proton is first abstracted, followed by liberation of X with a full octet of electrons. This mechanism was suggested by Drake and McElvain[72] for the removal of hydrogen bromide from ethyl β-bromopropionate in the presence of piperidine, and by Mills[73] for the removal of acetic acid from β-aldoxime acetates in the presence of alkali.

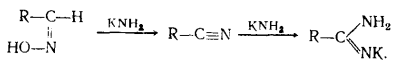
According to Hauser and coworkers[57,74], the removal of hydrogen chloride from aldochlorimines by various bases, and the splitting of benzaldehyde oxime di- and tri-nitrophenyl ethers observed by Brady[70,71], also proceed by the same mechanism.

O-Alkyl ethers of aldoxomes are converted into nitriles by the action of potassium amide in liquid ammonia[75]. The *O*-benzyl ether of α-benzaldehyde oxime decomposes into benzonitrile (some benzamide is also formed) and benzyl alcohol when heated with fused potassium hydroxide[76].

Jordan and Hauser had earlier found[77] that certain *anti*-aldoximes in solution in 2 *N* NaOH at 97–100° are slowly converted into a mixture of the corresponding carboxylic acids and the isomeric *syn*-aldoximes; the latter are also slowly converted into carboxylic acids. It was suggested that the carboxylic acids are formed by hydrolysis of the nitriles produced as intermediates in the dehydration of the *anti*-aldoximes.

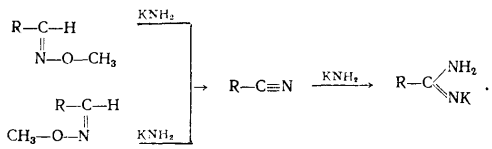
Vermillion and Hauser investigated the action of potassium amide on certain *syn*- and *anti*-aldoximes and their *O*-methyl ethers and acetyl derivatives[75].

After 9 d in a sealed tube with potassium amide in liquid ammonia at room temperature, *anti*-4-methoxybenzaldehyde oxime produces 4-methoxybenzamidine (48%) and 4-methoxybenzamide (15%). Under the same conditions the corresponding *syn*-aldoxime is apparently partly decomposed, but no products were isolated. The formation of the amidine from the *anti*-aldoxime is apparently due to the loss of water with formation of the nitrile, which then reacts with the potassium amide:



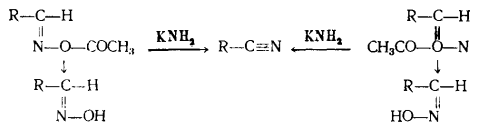
In fact, the nitriles are rapidly converted into amidines in the presence of potassium amide in liquid ammonia. The amides are probably produced by hydrolysis of the amidines, and possibly also directly from the nitriles by reaction with the potassium hydroxide produced by the action of potassium amide with the water split off from the *anti*-aldoximes.

Vermillion and Hauser also found that in the presence of potassium amide in liquid ammonia the *O*-methyl ethers of both *syn*- and *anti*-4-methoxybenzaldehyde oximes split off the elements of methanol to form 4-methoxybenzonitrile, which under the reaction conditions is completely or partially converted into the corresponding amidine:



With reaction for 2 h in the presence of 1.28 equiv. potassium amide, the *anti*-ether is fully decomposed, but the *syn*-ether only partially; the removal of the elements of methanol proceeds more readily from the *anti*-form than from the *syn*-form of the ether, as would be expected. The elimination from the *anti*-ether may be substantially complete within a few minutes. With 3 equiv. of potassium amide, the *syn*-ether is fully decomposed in 4 h, giving the amidine in a yield of ~ 90%.

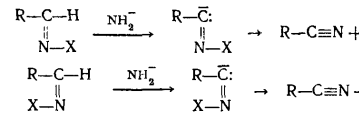
The acetyl derivatives of *syn*- and *anti*-benzaldehyde oximes react with potassium amide in liquid ammonia to form a mixture of the nitrile with the corresponding benzaldehyde oxime:



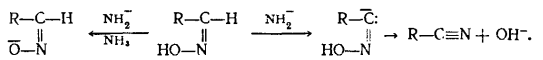
With reaction for 10 min at -33° *anti*-4-methoxybenzaldehyde oxime acetate gave yields of nitrile and aldoxime of 87% and 4% respectively; the corresponding *syn*-compound gave nitrile and aldoxime yields of 25% and 61% respectively. As would be expected, the yields of nitrile from the *anti*-acetates are higher, and the yields of aldoximes lower, than from the isomeric *syn*-acetates. It is of interest that the *syn*-acetates are not isomerised into the *anti*-forms by the action of potassium amide in liquid ammonia, and consequently the formation of nitriles from the *syn*-acetates is the result of direct removal of the elements of acetic acid, without preliminary isomerisation into the *anti*-acetates.

As compared with sodium hydroxide, which reacts with most *syn*-acetates to form substantially only the *syn*-aldoximes, potassium amide allows more of the β-elimination and less of the hydrolysis, giving a considerable amount of nitrile with *syn*-acetates also.

Vermillion and Hauser consider that the loss of HX from *syn*- and *anti*-aldoximes and their *O*-methyl ethers and acetyl derivatives by means of potassium amide is caused by attack by the base on the aldehydic hydrogen, which comes off as a proton; this is followed by the elimination of X as the anion with formation of the nitrile:

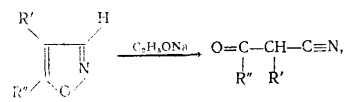


The elimination of water from an *anti*-aldoxime in the presence of potassium amide may be represented as follows:



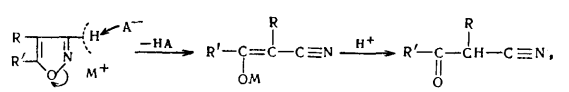
Here the base undoubtedly reacts with the hydroxyl hydrogen to give the aldoxime salt, but this salt is in equilibrium with unchanged aldoxime. This dehydration by means of bases is of particular interest since it proceeds by abstraction of the proton attached to carbon, although this proton is less active than that attached to the oxygen.

The cyclic analogues of the aldoximes — the 3-unsubstituted isoxazoles — can undergo ring-opening to form ketonitriles by the action of nucleophilic reagents, under conditions very similar to those of the aminonitrile rearrangement of quaternary pyrazolinium and aldehyde hydrazonium salts:



where R', R" = H, alkyl, aryl, etc.

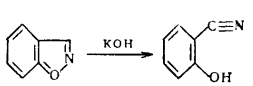
The nucleophilic opening of the isoxazole ring has been much studied[78-80]. Its mechanism involves initial abstraction of a proton from the 3-carbon atom followed by the substantially irreversible isomerisation of the resulting ion into the enolate ion of the end-product[78,80]:



where M = Na, K; A = OH^-, OR^-, NH_2^-.

Pino and coworkers showed that this reaction goes to completion, and is of the first order[81].

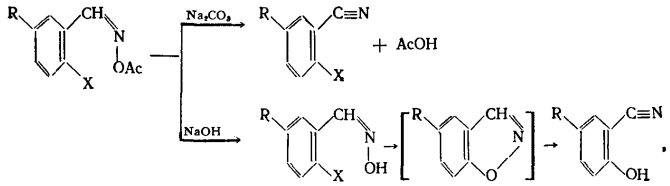
4,5-Benzoisoxazole is particularly unstable towards alkalis; when dissolved in potassium hydroxide it decomposes to salicylonitrile[82]:



The same product is obtained when 4,5-benzoisoxazole is heated[83].

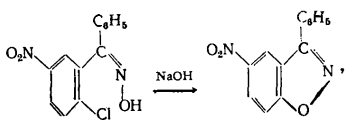
Treatment of the acetyl derivative of 2-chloro-5-nitro-β-benzaldehyde oxime with sodium carbonate eliminates acetic acid, with formation of the corresponding nitrile[84]. The action of sodium hydroxide on this oxime (and on 2-chloro-, 2-bromo- and 2-iodo-β-benzaldehyde oxime[85])

converts it into the nitrile, the halogen atom being replaced by the OH group. The reaction proceeds through the intermediate formation of the 3-unsubstituted nitrobenzoisoxazole, which here is unstable and cannot be isolated:



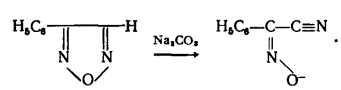
where R = H, NO_2; X = Cl, Br, I.

The action of sodium hydroxide on 2-chloro-5-nitrobenzophenone oxime produces 5-nitro-3-phenylbenzoisoxazole[86]:

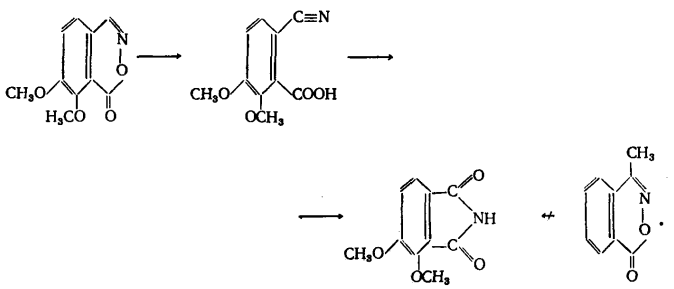


but this does not undergo further rearrangement, since the hydrogen atom in position 3 has been replaced by the phenyl group.

Furazans decompose analogously to the isoxazoles[87], cyanoketoximes being obtained even by the action of sodium carbonate solution:



Brady and coworkers have observed similar reactions in the benzo[*d*]oxazine ring[88]; the anhydride of the oxime of opianic acid forms the nitrile on gentle heating and the imide 3,4-dimethoxyphthalic acid on further heating:

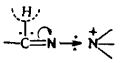


Under comparable conditions 4-methylbenzo[*d*]oxazin-1-one does not give the phthalimide, since the methyl group occupies the position of the hydrogen atom on the C=N double bond, and the formation of the nitrile is impossible.

4. STRUCTURAL FACTORS DETERMINING THE POSSIBILITY OF NITRILE REARRANGEMENTS

As is seen from the material above, the nitrile fission of N–N, N–O, and N–Cl bonds has been observed under very diverse experimental conditions. Most frequently the rearrangement requires the action of a strong nucleophilic reagent, and the part played by such a reagent is clear: it causes deprotonation of the aldehydic carbon atom and so facilitates or induces the reaction.

The nitrile rearrangement occurs only in compounds in which the N–N (or N–O) bond is strongly polarised[11,76]. This polarisation is strongest in compounds containing a quaternary nitrogen atom, such as quaternary pyrazolinium[15,38,48–50], dihydrophthalazinium[54] and hydrazonium salts[6,55,59–61], which are typically ionic compounds carrying a full positive charge on the terminal nitrogen atom of the grouping $-CH=N-\overset{+}{N}\!\!<$. This charge attracts towards itself the pair of σ electrons forming the N–N bond, that is, it induces polarisation of the nitrogen–nitrogen bond, which in its turn produces a considerable shift of the π electrons of the C=N double bond, which leads to increased lability of the proton on the carbon atom:



The deprotonation proceeds readily in aqueous alkaline solution, by the action of the hydroxide ions. As a result of this twofold action (polarisation of the N–N bond and the action of the nucleophilic reagent) nitrile fission proceeds very readily, usually at room temperature.

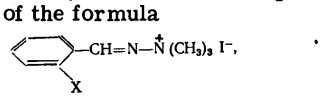
It is of interest to note here that where there is a single action (thermal fission of quaternary hydrazonium or pyrazolinium salts or pyrazolinium chlorides) the reaction requires much more severe conditions[6,12,13,15].

In other instances the necessary polarisation of the N–N bond is produced by including some cationoid activity on the terminal nitrogen atom, by substituting it with electron-withdrawing groups (phenyl, acetyl, benzoyl, etc.) or by increasing this cationoid activity by means of complex-forming agents, or by protonisation.

In particular, for nitrile fission of substituted aldehyde hydrazones of structure $RCH=N-NR'R''$, the substituents R′ and R″ may be groups which facilitate polarisation and cleavage of the N–N bond under the experimental conditions; however, if $R' = R'' = CH_3$, the $+I$-effect of the methyl groups prevents this polarisation (hence benzaldehyde dimethylhydrazone is stable to boiling with solid potassium hydroxide or sodium amide[6,11,33]).

Activation of the $-CH=N-N\!\!<$ (or $-CH=N-O-$) grouping may generally be accomplished in two ways, since the ease with which it dissociates increases (*i*) with the strength of polarisation of the N–N (or N–O) bond, and (*ii*) with the ease of deprotonation of the carbon atom in the β position to the sp^3 nitrogen atom. The former is best achieved by creating the maximum positive charge on the sp^3 nitrogen atom; the influence of this charge is then transmitted through the C=N double bond and facilitates deprotonation of the carbon atom.

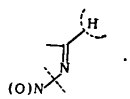
The deprotonation is also facilitated by the introduction of electron-accepting groups near this carbon atom, as in shown, in particular, by the data of Smith and Walker[55] who, as mentioned above, established that quaternary hydrazonium salts of the formula



containing an electron-accepting substituent in the benzene ring (X = NO_2 or Cl), this substituent increasing the acidity of the β-hydrogen atom, form the corresponding benzonitrile even when boiled in aqueous solution. However, the unsubstituted compound, or one containing an electron-donating group such as *p*-dimethylamino, undergo hydrolysis as well as β-elimination, to give a mixture of nitrile and aldehyde.

We have already remarked that the presence of electron-accepting substituents in the benzene ring of aromatic chloroimines also increases the rate of their nitrile fission[57] and, finally, it is known that the introduction of electron-accepting substituents (for example, the nitro-group) into position 4 of the isoxazole ring greatly increases its reactivity towards alkaline reagents[89,90].

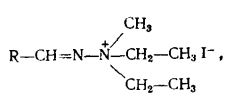
In considering the nitrile fission of oximes and their *O*-substituted derivatives, it must be borne in mind that trans-elimination is the more easily achieved, that is, the *anti*-isomers are the more reactive. We note that in the fission of the pyrazoline, pyrazole, or isoxazole ring, the structure of the heterocycles is such that it is trans-elimination which occurs here also:



The similarity between the nitrile rearrangement of quaternary pyrazolinium and aldehyde hydrazonium salts and the Hofmann degradation of quaternary ammonium bases has been repeatedly remarked[6,11,38,54,61].

Ioffe and coworkers have noted[51,61] that although the aldehyde hydrazonium salts which they investigated contained two ethyl groups (they used diethylhydrazones), which are the most readily removed in the Hofmann degradation, they never observed the formation of ethylene; consequently, the nitrile formation proceeds much more readily than the Hofmann decomposition with elimination of the β-hydrogen atom in the structure $CH_3-CH_2-\overset{+}{N}<$.

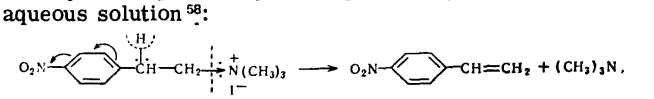
In compounds of the structure



the positive charge on the quaternary nitrogen atom causes strong polarisation of the $C-\overset{+}{N}$ bonds and the $N-\overset{+}{N}$ bond. Naturally, insofar as the molecule is potentially able to undergo either nitrile formation or Hofmann degradation, the β-elimination will occur in the direction in which the β-hydrogen atom is most readily removed. Clearly, the effect of the positive charge on the nitrogen atom is much more readily transmitted across the C=N double bond to the aldehydic hydrogen atom than to the β-hydrogen atoms of the ethyl groups, and this is why the nitrile rearrangement is the reaction that occurs here, and, for the same reasons, why quaternary pyrazolinium salts carrying β-hydrogen atoms in both position 3 and position 4 undergo nitrile formation and not Hofmann degradation.

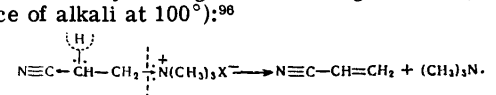
Even electron-accepting groups (nitrile or phenyl) in the β position of the ethyl radical in quaternary *N*-ethylpyrazolinium salts do not facilitate the Hofmann degradation of the C–N bond; here also the pyrazoline ring opens, with formation of β-dialkylaminopropionitriles[91].

Nevertheless, instances are known where the Hofmann degradation of quaternary ammonium bases proceeds as readily as the aminonitrile rearrangement, when the structure of the compounds is such that elimination of the β-hydrogen atom is facilitated. Thus salts of quaternary ammonium bases containing the phenylethyl group decompose when heated with aqueous alkali[92-94]. Moreover, according to von Braun[95], steam distillation of trimethyl-(2-phenylethyl)ammonium hydroxide causes it to decompose almost quantitatively to give styrene. However, aqueous solutions of trimethyl-(3-phenylpropyl)ammonium and other ammonium hydroxides in which the phenyl radical is further removed from the β-hydrogen atom can be evaporated on a water-bath with no sign of decomposition. Finally, trimethyl-2-(*p*-nitrophenyl)ethylammonium iodide readily decomposes to produce *p*-nitrostyrene even in aqueous solution[58]:

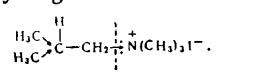


This is because of the influence of the *p*-nitrophenyl group adjacent to the β-carbon atom; the inductive and electromeric effects of this group both act in the same sense, greatly facilitating elimination of the β-hydrogen atom.

In quaternary ammonium salts derived from β-dialkylaminopropionitriles, removal of the β-hydrogen atom is facilitated by the inductive effect of the nitrile group; these salts readily undergo Hofmann degradation (in the presence of alkali at 100°):[96]



On the other hand, if the β-carbon atom carries alkyl groups, the rate of this reaction decreases[97], since the +*I*-effect of such groups compensates for the inductive effect of the positively charged nitrogen atom, and hinders elimination of the hydrogen atom:



Here, hydrolysis competes successfully with the β-elimination in an aqueous alkaline medium, so that the Hofmann degradation of such quaternary ammonium salts is usually carried out by heating with silver oxide or solid alkali.

The influence of inductive and electromeric factors on elimination reactions has been investigated by Hughes and Ingold[58,98]. An analogous analysis of the influence of structural factors provides an understanding of the possibility and varying ease of accomplishment of nitrile rearrangements.

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SELECTIVE REDUCTION OF ALIPHATIC NITRO-COMPOUNDS WITH OTHER FUNCTIONAL GROUPS

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I. INTRODUCTION

In recent years there has been a great development of the chemistry of aliphatic nitro-compounds. The improvement of old and the discovery of new methods of synthesis has led to a sharp increase in the number of nitro-products that have become readily available; some of these are already produced on the industrial scale.

The nitroalkanes, which are now manufactured in tens of thousands of tons a year, are used as starting materials in the production of many aliphatic nitro-compounds.

In this connection, the attention of chemists has been increasingly attracted to the possibility of using nitro-derivatives of the aliphatic series for the needs of industry and agriculture, both directly and as a relatively cheap chemical material for the synthesis of various products with important applications.

Reduction occupies a special position in the chemical transformations of nitro-compounds. There is no need to dwell on the tremendous importance of this reaction in the aromatic series. However, the reduction of aliphatic nitro-compounds has been studied in a less detailed manner and the literature on this question has not been specially systematised. Isolated information on some particular problems may be found in a number of monographs and review articles on the nitro-compounds[1-7].

Since the question of the reduction of nitro-compounds containing other functional groupings in addition to the nitro-group is of fundamental chemical and pratical interest, only examples of selective reduction of aliphatic functional nitro-compounds will be considered in this review. This question is considered in two aspects. Thus, in the first part the reduction of the nitro-group to the amino-group without change of other functions is considered, and in the second the reduction of functional groups without changing the nitro-group.

It was not our purpose to produce an exhaustive review of all instances of selective reduction of nitro-compounds, and the material of the review has been selected in such a way as to illustrate the use of various reducing agents or catalysts, suitable for the selective (in the above sense) reduction of functional aliphatic nitro-derivatives.

II. SELECTIVE REDUCTION OF THE NITRO-GROUP IN ALIPHATIC NITRO-COMPOUNDS WITH OTHER FUNCTIONAL GROUPS

1. Reduction of Nitro-Alcohols to Amino-Alcohols

Of all aliphatic nitro-compounds, the reduction of the nitro-alcohols has been most fully studied. The leading motive of many investigations in this field is the wide use

of amino-alcohols in a number of branches of industry and also their great importance as physiologically active compounds.

The selective reduction of nitro-alcohols does not present particular difficulties, because the hydroxyl group is inert to the action of the majority of chemical reagents usually employed for reducing the nitro-group.

Hydrogenation with Raney nickel is one of the main methods of selectively reducing nitro-alcohols. Change of temperature between 30° and 100° and of pressure between 1 and 130 atm has no material effect on the yields of amino-alcohols [8-20]; however, carrying out the hydrogenation in the presence of carbon dioxide leads to a significant increase in the yield of amino-alcohols [11,14]. In an acid medium, as a rule, the hydrogenation of the nitro--group is not accompanied by side-reactions. On the other hand, when the reaction is carried out in an alkaline medium, the reduction is frequently accompanied by side--reactions connected with the instability of nitro-alcohols under these conditions. Thus in the reduction of 2-methyl--2-nitropropan-1-ol with Raney nickel in liquid ammonia, Johnson separated 1,2-diamino-2-methylpropane, the appearance of which the author explains by the exchange of a hydroxyl group of the reduced alcohol for an amino--group [21]. Moreover, in an alkaline medium methyl groups are easily eliminated from tertiary carbon atoms. For example, in the reduction of 2-ethyl-2-nitropropan-1,3--diol, 2-aminobutanol and methanol are formed [22]. In an acid medium the reaction proceeds normally and leads to the formation of 2-amino-2-ethylpropan-1,3-diol.

In a number of papers the reduction of nitro-alcohols (monohydroxy- and polyhydroxy-) to amino-alcohols in the presence of platinum oxide [23-25] and palladium [26-29] is described. Usually the yield of amino-alcohols is 80–95%. The process is best carried out in an acid medium.

Fundamental information on the selectively catalytic hydrogenation of nitro-alcohols is collected in Table 1.

There are many papers on the reduction of nitro-alcohols by chemical reagents. The reduction of nitro-alcohols with nascent hydrogen has been studied in great detail. Various combinations of metals and acids have been proposed as a source of hydrogen (for example, Fe + H_2SO_4, HCl, or H_3PO_4 [10,30,31]; Zn + HCl [14]; $SnCl_2$ + HCl [15]).

TABLE 1.

Initial nitro-alcohol	Catalyst*	Hydrogenation conditions (temp., H_2 pressure)	Solvent	Yield of amino--alcohol, %	Ref.
2-Methyl-2-nitropropan--1-ol	Ni/Re	70°; 30–35 atm	water–methanol	95.8	9
2-Nitro-1-phenylpropan--1-ol	Ni/Re	50–70°; 20–120 atm; CO_2	alcohol	87.45 (no CO_2)	14
1-Cyclohexyl-2-nitro-ethan-1-ol	Ni/Re	25–35°; 4–6 atm; CO_2	–	91	16
$CH_2OH-C(NO_2)CH_2OH$ | C_nH_{2n+1}	Ni/Re	125°; 1–135 atm	water–methanol	–	18
1,4-Dinitrobutan-2,3-diol	Ni/Re	40–80°; 200 atm	dioxan	–	19
1-Deoxy-1-nitro-D--*manno*-D-galaheptanol	Ni/Re	20°; 1 atm	–	90	16
1,4-Dideoxy-1,4-dinitro-neoinositol	Ni/Re	20°; 1 atm	acetic acid–dimethylform-amide	89.6	20
2-Nitrooctadecan-1,3--diol	PtO_2	20°; 1 atm	acetic acid	71	24
3-Nitropentan-2,4-diol	5% Pd on $BaSO_4$	20°; 1 atm	H_2O + pyridine	86.5	28
2-Nitropropan-1,3-diol	Pd on $BaSO_4$	20°; 1 atm	in the presence of COOH–COOH	93	2,9

* Ni/Re presumably denotes Raney nickel (Ed. of Translation).

Evidently, the action on β-nitro-alcohols of iron in sulphuric acid at a pH of 3–3.5, and the use of 1–1.1 equivalents of acid for each nitro-group give the most favourable conditions for the reduction of β-nitro-alcohols by this method; the yields of amino-alcohols is 92–98%.

Lower β-amino-alcohols (C_3–C_5) are conveniently obtained by the action of aluminium in weak acid on nitro--alcohols [32]; the yield varies between 50 and 70%. The method is particularly recommended for nitro-alcohols sensitive to strong alkalis and acids, but the effectiveness of the method is greatly reduced in the reduction of higher nitro-alcohols (>C_5).

The reduction of β-nitro-α-phenyl-alcohols to the corresponding amino-derivatives by sodium amalgam [33] and lithium tetrahydroaluminate [34] has also been described.

As has been shown by the investigations of Jenny and Druey [35], and also by Grob and Gadient [36], lithium tetrahydroaluminate, or zinc and hydrochloric acid, or aluminium and acetic acid may be used for the simultaneous reduction of nitro-groups and multiple carbon bonds in higher aliphatic unsaturated nitrodiols. The yields of saturated amino-alcohols vary between 40 and 70%. According to Takagi and coworkers [37], ammonium amalgam reduced nitrodiols to hydroxylaminodiols [37].

Examples are known of the selective electrochemical reduction of nitro-alcohols and diols [17,38]. The authors used a lead cathode and dilute sulphuric or hydrochloric acid as electrolytes. The yield of amino-derivatives was 75–94%.

2. Reduction of Alkyl Ethers of Nitro-Alcohols to Alkyl Ethers of Amino-Alcohols

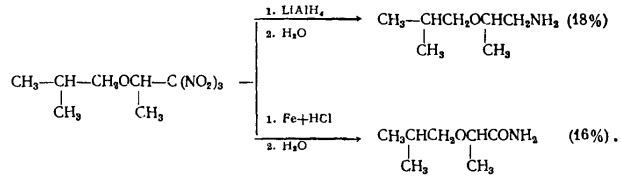
The alkoxy-group in the β-position to the nitro-group is much more stable than the hydroxyl group. Thus, when lithium tetrahydroaluminate acts on β-nitro-α-phenyl-alcohols the carbon–carbon bond is ruptured, but when the analogous alkoxy-compounds are reduced with this reagent, the corresponding β-alkoxy-β-phenylamines are formed in quantitative yield [34].

It is very easy to reduce 1-alkoxy-2-nitro-1-phenyl-alkanes by zinc in organic acids. For example, by using zinc and formic acid, it is possible to obtain β-amino--ethers in ~90% yield [39]. Lambert and coworkers, who made a detailed study of the action of various reducing agents on lower aliphatic β-nitro-ethers, showed that the highest yields of amino-ethers are obtained by catalytic hydrogenation [40]:

$$C_2H_5OCH_2CH_2NO_2 \xrightarrow[20°,\ 100\ atm,\ alcohol]{H_2/PtO_2} C_2H_5OCH_2CH_2NH_2 \quad (52\%),$$

$$CH_3CH(NO_2)CHCH_3 \xrightarrow[50°,\ alcohol]{H_2,\ Raney\ Ni} CH_3CH(NH_2)CHCH_3 \quad (50\%).$$
$$\quad\quad\quad

Schechter and Cates reduced isobutyl 1-trinitromethylethyl ether to the corresponding amine by the action of lithium tetrahydroaluminate, and to α-isobutoxypropionamide by the action of iron in hydrochloric acid[42].



3. Reduction of Nitro-Ketones and Nitro-Aldehydes to Amino-Ketones and Amino-Aldehydes

The presence of a carbonyl group in nitro-compounds makes selective reduction of the nitro-group difficult, because many hydrogenation catalysts and chemical reagents (for example, lithium tetrahydroaluminate) first reduce the carbonyl group. Moreover, reduction is often accompanied by cyclisation through the carbonyl group of the amino-ketones and -aldehydes formed.

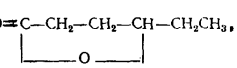
Using 4-keto-6-nitrohexanoic acid (II) and its esters as examples, Moldenhauer[43] and Grundmann[44] showed the possibility of selectively reducing the nitro-group in β-nitro-ketones. When (II) was hydrogenated with palladium on charcoal in hydrochloric acid under normal conditions, the yield of amino-acid reached 96.4%.[44]

$$\underset{\text{(II)}}{CH_2(NO_2)CH_2CO[CH_2]_2COOH} \rightarrow \underset{\text{(III)}}{CH_2(NH_2)CH_2CO[CH_2]_2COOH}.$$

However, hydrogenation of (II) with palladium on barium sulphate in acetic acid leads to (III) in lower yield (67%).

The authors point out the instability in an alkaline medium of compounds containing the β-amino-ketone grouping.

The possibility of selectively reducing the nitro-group in esters of (II) has also been studied and it has been shown that it may be effected by hydrogenation with 5% palladium on charcoal in water[43]. The yield of the corresponding esters of the amino-keto-acid mounted to ~30%. The use in this reaction of Raney nickel as hydrogenation catalyst at low hydrogen pressures leads to the formation of (III) in 20% yield, but at a pressure of 100 atm and a temperature of 225–240° the lactone



is formed in 33.7% yield[44].

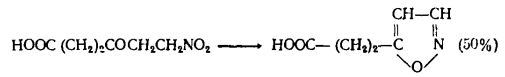
Hydrogenation of (II) with platinum dioxide in water brings about reduction of the keto-group as well as the nitro-group and leads to 6-amino-4-hydroxyhexanoic acid[43].

When palladium on aluminium oxide is used as catalyst, deamination of the reduction products occurs[43]:

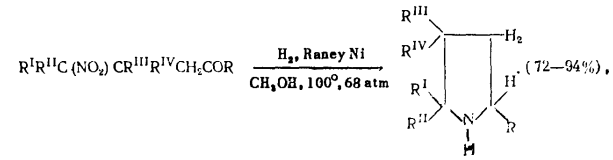
$$CH_2(NO_2)CH_2CO(CH_2)_2COOR \longrightarrow CH_3CH_2CO(CH_2)_2COOR \quad (20\text{–}30\%)$$

where R = H or alkyl.

When lithium tetrahydroaluminate acts on (II), all the functional groups are reduced[43]. Reduction of (II) with tin(II) chloride in hydrochloric acid leads to the formation of an isoxazole ring[45]:



According to Kloetzel[46], on reduction γ-nitro-ketones undergo ring closure to pyrrolidine rings:

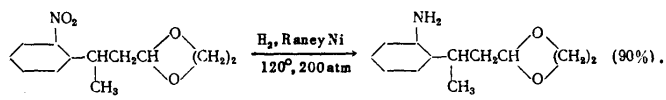


where R, R^I, R^{II}, R^{III}, R^{IV} = H or alkyl.

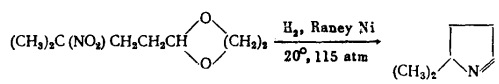
In connection with the difficulties arising in the direct reduction of nitro-ketones and nitro-aldehydes, it is useful to first protect the keto-group by the formation of acetals. Losanitsch[47] has described the reduction of the nitro-group in β-nitroacetals by sodium in boiling alcohol:

$$NO_2CH_2CH(OC_2H_5)_2 \longrightarrow NH_2CH_2CH(OC_2H_5)_2 \quad (\sim 50\%).$$

However, when acetals of γ-nitro-ketones are reduced, the final product largely depends on the structure of the initial nitro-acetal. Thus, in particular, reduction of the acetal† of ethylene glycol and γ-(2-nitrocyclohexyl)butyraldehyde is not accompanied by cyclisation of the final product[48]:



On the other hand, hydrogenation of the acetal‡ of ethyleneglycol and γ-methyl-γ-nitrovaleraldehyde is accompanied by cyclisation[49]:



4. Reduction of Nitro-Acids and Their Derivatives to Amino-Acids and Derivatives

The tremendous practical interest in the selective reduction of the nitro-group in α-nitro-acids and their derivatives as a method of synthesis of α-amino-acids should be mentioned.

The world demand for some amino-acids now reaches some hundreds of thousands of tons per year; for this reason at the present time intensive searches are being

† 2-[2-(2-Nitrocyclohexyl)propyl]-1,3-dioxolane (Ed. of Translation).

‡ 2-(3-Methyl-3-nitrobutyl)-1,3-dioxolane (Ed. of Translation).

made for cheap chemical materials which could be used in their synthesis. In particular, great attention has been paid to the possibility of using nitromethane for this purpose. Nitroacetic esters can easily be obtained from nitromethane, and from these the synthesis of many amino-acids can be effected. Thus, glycine was obtained by the reduction of nitroacetic ester on Raney nickel[50].

In a general way the synthesis of α-amino-acids from nitromethane may be represented by the following scheme:

$$CH_3NO_2 \rightarrow CH_2NO_2COOR' \rightarrow RCH(NO_2)COOR' \rightarrow RCH(NH_2)COOH,$$

where R = alkyl, or substituted alkyl; R′ = CH_3 or C_2H_5. Using this scheme, Weisblat and coworkers[51] synthesised DL-tryptophan and leucine.

In recent years the selective reduction of α-nitro-acids obtained from nitroacetic ester has been studied in detail by Belikov and coworkers[52-54]. In particular, in a study of the hydrogenation of methyl esters of α-nitro-αβ-unsaturated acids with Raney nickel in methanol, it was shown that sometimes there is first addition of the elements of the solvent through the activated double bond, which is probably catalysed by traces of alkali present in the catalyst[52]:

$$CH_3CH{=}C(NO_2)COOCH_3 \xrightarrow{CH_3OH} CH_3CHCH(NO_2)COOCH_3 \rightarrow$$
$$\rightarrow \underset{55^\circ,\,75\ atm}{\xrightarrow{H_2}} CH_3CHCH(NH_2)COOH \quad (41\%).$$
$$\quad OCH_3 \qquad\qquad\qquad\quad OCH_3$$

Esters of sterically hindered α-nitro-acids are normally reduced under these conditions:

$$(CH_3)_2CH{-}CH{=}C(NO_2)COOCH_3 \xrightarrow[50^\circ,\,68\ atm]{H_2,\,CH_3OH} (CH_3)_2CHCH_2CHCOOCH_3 \quad (61\%).$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NH_2$$

Another example is the synthesis of proline from nitroacetic ester[54]:

$$CH_2NO_2COOCH_3 \xrightarrow{CH_2{=}CH{-}CHO} HCCH_2CH_2CH(NO_2)COOCH_3 \rightarrow$$
$$\rightarrow (CH_3O)_2CHCH_2CH_2CH(NO_2)COOCH_3 \xrightarrow[2.\ H_2O]{1.\ H_2/PtO_2} \text{(proline)}$$

Reduction of α-nitro-acids or their derivatives to amino-acids with the aid of chemical reagents is carried out much less frequently; as a rule, the amino-acids are obtained in a lower yield than by catalytic hydrogenation. Information on the reduction of nitro-acids and their derivatives is given in Table 2.

Sometimes the hydrogenation of nitro-acids is accompanied by side reactions. Thus, the reduction of esters of dibasic γ-nitro-acids on platinum oxide or Raney nickel leads to lactams[61] and other cyclic products[62]:

$$CH_3OOC(CH_2)_2CH(CH_2)_2COOCH_3 \xrightarrow[25^\circ,\,2\text{–}3\ atm]{H_2,\,PtO_2} (CH_2)_2{-}COOCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH{-}NH\diagdown C{=}O$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2{-}CH_2\diagup$$
$$\qquad\qquad\qquad\quad NO_2$$
$$\xrightarrow[275^\circ,\,250\text{–}350\ atm]{H_2,\ Raney\ Ni} \text{(pyrrolidine)} \quad (57\%).$$

When the ethyl 3,4-dehydro-5-nitrohexanoate is hydrogenated on Raney nickel at high temperatures and pressures, caprolactam is obtained instead of ethyl 6-amino-hexanoate[62].

Isolated information on the reduction of nitro-acids containing other functional groups is given in preceding and subsequent parts of Section II (see pp. 21,23).

5. Reduction of Nitro-Nitriles to Amino-Nitriles

The selective reduction if the nitro-group in nitro-nitriles to the amino-group is of considerable interest, since in the end it opens the way to the synthesis of amino-acids.

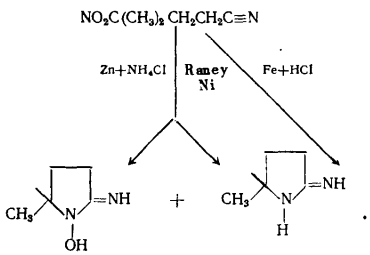
Using nitro-t-butyl cyanide as an example, Buckley and coworkers[63] showed that the selective reduction of β-nitro-nitriles is usefully carried out with iron in dilute hydrochloric acid. The yield of amino-t-butyl cyanide was 65%. When the starting material and other β-nitro-nitriles were catalytically hydrogenated (Raney nickel, palladium on calcium carbonate), instead of amino-nitriles the authors obtained amino-acid amides, diamines, and other secondary products.

As Buckley and Elliott showed[64], when γ-nitro-nitriles are reduced both by chemical and catalytic methods amino-nitriles are generally not obtained. Instead of them,

TABLE 2.

Initial nitro-acid or its derivative	Reducing agent or hydrogenation catalyst	Reaction conditions	Solvent	Reduction product	Yield, %	Ref.
Ethyl β-indolyl-α-nitropropionate	Raney Ni	100°, ~100 atm	alcohol	DL-tryptophan	50	55
Diethyl α-nitroglutarate	Raney Ni	100°, 150 atm	alcohol	DL-glutamic acid	–	56
$(CH_3O)_2CH(CH_2)_2CHCOOCH_3$ (NO₂)	skeleton Ni	70°, 62 atm	absolute methanol	$(CH_3O)_2CH(CH_2)_2CHCOOCH_3$ (NH_2)	75	54
Ethyl αα-dimethyl-β-nitropropionate	Raney Ni	90°, 95 atm	water + $Ba(OH)_2$	β-amino-αα-dimethylpropionic acid	65	57
$(CH_3)_2C(NO_2)(CH_2)_2$–CONRR′	Raney Ni	125°, 68 atm	–	$(CH_3)_2C(NH_2)(CH_2)_2CONRR'$	45–89	58
Methyl β-hydroxy-α-nitrobutyrate	5% Pd/C	20°, 40–50 atm	acetic acid	DL-threonine	74	53
$CH_3CH{=}C(NO_2)COOCH_3$	PtO_2	5°, 1 atm	ethyl acetate	$CH_3CH_2CH(NH_2)COOCH_3$	63	53
γ-Nitropentanoic acid	PtO_2	20°, 1 atm	alcohol	γ-aminopentanoic acid	98	59
$(CH_3O)_2CH(CH_2)_2CHCOOCH_3$ (NO_2)	PtO_2	20°, 60 atm	70% CH_3COOH	DL-proline	65	54
Ethyl β-indolyl-α-nitropropionate	Fe + HCl	20°	–	DL-tryptophan	25	55
Ethyl nitromalonate	Zn + CH_3COOH	50–80°	$(CH_3CO)_2O$	$CH_3CONHCH(CO_2C_2H_5)_2$	30	60

mixtures of the corresponding *N*-hydroxy-5-iminopyrrolidines and 5-iminopyrrolidines are obtained. For example:



6. Reduction of Nitro-Amines to Polyamines

Information in the literature relates to the reduction of β-nitro-amines, products readily obtained by the Mannich reaction from nitro-compounds, formaldehyde, and amines. The most selective reduction of the nitro-group in nitro--amines should, of course, not present any difficulties. However, in selecting the reaction conditions it should be noted that the process is often complicated by side-reactions which are connected with the instability of the initial compounds and to a large degree depend on the structure of the latter, the pH the medium, and other factors.

Johnson[65] reduced a series of β-nitro-amines on Raney nickel at 30–50° and a hydrogen pressure of 70 atm in methanol; the yield of diamines was 65–80%. A few other papers have been published on the selective reduction of nitro-amines and nitro-diamines on Raney nickel under similar conditions[66,67,70–72]. However, Senkus hydrogenated *NN*-diisopropyl-2-methyl-2-nitropropylamine under the same conditions and obtained a mixture of lower amines instead of the diamine[69]. The author explains this result by the instability of the initial nitro-amine. Some β-nitro-amines may be reduced to diamines by the action of tin(II) chloride in hydrochloric acid at 0° in yields of ~30%.[68]

When esters of α-nitro-β-alkylamino-acids are catalytically hydrogenated, esters of the αβ-diamino-acids are not obtained; the bond between the α- and β-carbon atoms is ruptured[70]:

$$\begin{matrix}RCH{-}CH(NO_2)COOR'\\ \quad\quad|\\ \quad\quad NHR'\end{matrix} \xrightarrow[PtO_2]{H_2} RCH_2NHR' + CH_2(NH_2)COOR'.$$

Dornow and Gellrich[34] observed similar cleavage of the initial α-nitro-β-alkyl aminoester under the action of lithium tetrahydroaluminate:

$$\begin{matrix}Cl{-}C_6H_4{-}CHCH(NO_2)COOC_2H_5\\ \quad\quad\quad\quad|\\ \quad\quad\quad\quad NHC_6H_5\end{matrix} \xrightarrow{LiAlH_4} Cl{-}C_6H_4{-}CH_2NHC_6H_5 + CH_3NH_2CH_2OH.$$

Obviously, this reaction is general for all β-nitro-amines in which the nitro-group is on the carbon atom connected to the ester grouping.

The reduction of the nitro-group in *N*-nitro-amines has been studied in the literature with nitroguanidine as an example. The catalytic reduction has been described of nitroguanidine to aminoguanidine with the aid of Raney nickel[71], platinum oxide[71,72], sodium with the addition of ammonium chloride in liquid ammonia[73], zinc dust[74–76], titanium trichloride[77,78]; an electrolytic method has also been used[79,80].

Moreover, it has been shown that nitroguanidine can be converted into nitrosoguanidine[71,81].

There are also reports on the electrolytic reduction of nitrourea to semicarbazide on a platinum cathode[82].

7. Reduction of Halogeno-Nitro-Compounds to Halogeno--Alkylamines

Catalytic hydrogenation is generally used for the selective reduction of the nitro-group in γ-fluoronitroalkanes. In particular, Cook smoothly reduced 2-heptafluoropropyl--1-nitrobutane to the corresponding amine under mild conditions (20°, 4 atm) with the aid of Adams' catalyst[83]. In the same paper it is shown that selective hydrogenation of the nitro-group in fluoronitroalkanes, including those containing hydroxyl groups in the β-position to the nitro-group, can be effected with the aid of Raney nickel. It has also been noted that lithium tetrahydroaluminate in the reduction of the nitro-group and some other functions does not generally affect the C–F bond and permits the preparation of the corresponding polyfluoroamines in good yield.

The reduction of monochloro-β-nitroalkanes is most efficiently carried out with tin(II) chloride in hydrochloric acid[88]. Under these conditions 2-chloro-3-methyl-1--nitrobutane gave the corresponding β-chloroamine in 57% yield. However, when the starting compound is hydrogenated on Raney nickel, a mixture of amines and hydroxylamines difficult to separate is formed.

As already mentioned, β-alkoxy-γ-trichloronitroalkanes[41] and γ-trichloro-β-hydroxynitroalkanes[15] may also be selectively reduced to amines in high yields (50–70%) by tin(II) chloride and hydrochloric acid.

3-Amino-1,1,1-trichloropropan-2-ol was obtained[85] by the reduction of 1,1,1-trichloro-3-nitropropan-2-ol on Raney nickel at room temperature and pressures up to 10 atm. However, at a higher pressure (50 atm) and increased temperature (106°), one chlorine atom may be reduced in addition to the nitro-group[15]:

$$CCl_3CH(OH)CH_2NO_2 \xrightarrow[\text{in HCl}]{H_2} CHCl_2CH(OH)CH_2NH_2\cdot HCl \quad (34.7\%).$$

In the light of these results, it may be concluded that Raney nickel is unsuitable for the selective reduction of the nitro-group in γγγ-trichloronitroalkanes.

8. Selective Reduction of Nitro-Groups in Aliphatic Sulphur-Containing Compounds

Several papers have been published on the selective reduction of the nitro-group in β-nitroalkyl sulphides[86], β-nitroalkyl sulphones[86,87] and β-nitrosulphonic acids[88] by hydrogenation of the initial compounds in methanol on Raney nickel at room temperature, or slightly higher, and at atmospheric or higher hydrogen pressure. In a number of cases the corresponding amines are obtained in close to quantitative yield.

Gold and coworkers made a detailed study of the reduction of the nitro-group in salts of β-nitrosulphonic acids of the type $CH_2(NO_2)CHRSO_3H$ (R = H, CH_3, C_6H_5); $CH(NO_2)R{-}CH_2SO_3H$ (R = H, CH_3, C_2H_5); $CH(NO_2)(C_2H_5)CH(C_3H_7)SO_3H$.[89] The authors consider that the most efficient conditions of hydrogenation of the initial salt are with Raney nickel in

water at 30° and low pressures; the yield of β-aminosulphonic acids is greater than 90%. At increased hydrogenation temperature there is a reduction in the yield of β-aminosulphonic acids. Reduction of the above-mentioned compounds may also be carried out by iron in water in the presence of catalytic quantities of hydrochloric acid (the yield of β-aminosulphonic acids is greater than 80%), and also electrolytically on a lead cathode with 15% sulphuric acid as an electrolyte (the yield of β-aminosulphonic acids is 60%).

The reduction of 1-nitroethyl *p*-tolyl sulphide (IV) and sulphone (V) proceed anomalously[90]. When treated with Raney nickel or Adams' catalyst, (IV) is recovered unchanged, but (V) gives a mixture of products:

$$p\text{-}CH_3C_6H_4SO_2CH(NO_2)CH_3 \xrightarrow[\text{Raney Ni}]{H_2} \begin{cases} p\text{-}CH_3C_6H_4SO_2C(NOH)CH_3 & \text{(VI) (10\%)} \\ p\text{-}CH_3C_6H_4SO_2NH_4 & \text{(28\%)} \\ p\text{-}CH_3C_6H_4SO_2H & \text{(50\%).} \end{cases}$$
(V)

When (IV) is treated with lithium tetrahydroaluminate, (VIa) is obtained in low yield:

$$p\text{-}CH_3C_6H_4SCH(NO_2)CH_3 \xrightarrow{LiAlH_4} p\text{-}CH_3C_6H_4S\overset{\overset{NOH}{\|}}{C}CH_3 \quad (14\text{—}16\%).$$
(IV) (VIa)

It should be emphasised that the reduction of aliphatic nitro-compounds with lithium tetrahydroaluminate is hardly mentioned in the literature. From this point of view the example given here is of undoubted interest.

9. Reduction of Nitro-Alkynes to Amino-Alkynes

The selective reduction of the nitro-group in aliphatic acetylene nitro-diols is described in papers by Jenny[35] and by Grob[36]

$$R\text{—}C{\equiv}CCH(OH)CH(NO_2)CH_2OH \rightarrow R\text{—}C{\equiv}C\text{—}CH(OH)CH(NH_2)CH_2OH,$$
(VII, *a—f*) (VIII, *a—f*)

(*a*) R = n-C_6H_{17}; (*b*) R = n-$C_{10}H_{21}$; (*c*) R = n-$C_{12}H_{25}$; (*d*) R = n-$C_{14}H_{29}$; (*e*) R = $C_{16}H_{33}$; (*f*) R = $C_{18}H_{37}$.

With the action of zinc and hydrochloric acid on (VII, *c*), the yield of (VIII, *c*) amounted to 72%. When (VII, *f*) was reduced by aluminium in ether with the addition of a little water and acetic acid at room temperature, the yield of (VIII, *f*) did not exceed 45%. Aluminium amalgam was found to be unsuitable for the reduction of (VII). Hydrogenation of (VII) with palladium on lead carbonate, with palladium on carbon, or with lithium tetrahydroaluminate involves the triple bond§.

By the action of zinc or aluminium in acid on optically active (VII, *f*), the authors obtained (VIII, *f*) in optically active form.

10. Reduction of Nitro-Alkenes to Amino-Alkenes

There is evidently no general method for the selective reduction of the nitro-group in nitro-alkenes. The selection of the reducing agent and the reaction conditions depends entirely on the structure of the initial nitro-alkene. It is entirely understandable that special difficulties should be encountered in attempts to reduce the nitro-group without affecting the double bond in α-nitro-alkenes. The instability of the corresponding amino-derivatives considerably complicates the study of this reaction. However, even with exhaustive reduction of α-nitro-alkenes, it is necessary to choose carefully the reducing agent and the conditions of the reaction, since frequently oximes are obtained as the final product of the expected alkylamines. Thus, when aluminium and amalgam[91], zinc dust in an alkaline medium[92], or iron filings in hydrochloric acid[93] acts on α-nitro-alkenes only the oximes of the corresponding aldehydes and ketones are obtained. Ammonium sulphide reduces α-nitro-alkenes to acid amides[94]. When hydride reducing agents, for example, lithium tetrahydroaluminate, act on α-nitro-alkenes the double bond is first reduced[83]. The same result was obtained in attempts at selective electrolytic reduction[84].

Until recently only one α-nitro-unsaturated compound (ethyl β-methyl-α-nitrocrotonate) had been described in which the nitro-group had been successfully reduced selectively:

$$(CH_3)_2C{=}C\text{—}COOC_2H_5 \rightarrow (CH_3)_2C{=}C(NH_2)COOC_2H_5 \text{ or } (CH_3)_2C{=}C(NHCOCH_3)COOC_2H_5.$$
(IX) (X) (XI)

Obviously, the stability of the C=C bond in (IX) to reduction is related to the steric hindrance caused by its substituents.

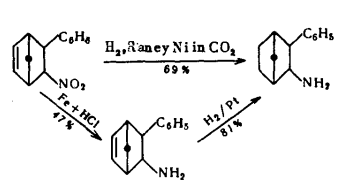
Bouveault[95] obtained (X) in 60–62% yield by the action of aluminium amalgam in ether on (IX), having shown that acid and alkaline reagents were not suitable for the selective reduction of (IX). However, these results were not confirmed by the later work of Süs, who only obtained the acetyl derivative (XI).[96] Moreover, he showed that the catalytic reduction of (IX) on Raney nickel at 70° and 50 atm in the presence of acetic anhydride leads to (XI) in over 90% yield[97].

In recent years Kuhn proposed a reducing agent which apparently can be used for the selective reduction of the nitro-group in α-nitro-alkenes[98]. According to the author, hydrazine in the presence of catalytic platinum or palladium is a very effective reducing agent for nitro- and nitrate-groups, and it does not affect the carbon–carbon double bond. In particular, 2-amino-1-phenylprop-1-ene can be obtained from 2-nitro-1-phenylprop-1-ene. Replacement of the platinum or palladium by nickel reduces the effectiveness and selectivity of the reagent and leads to hydrogenation of the double bond.

The selective reduction of the nitro-group in β-nitro-alkenes has not been described in the literature.

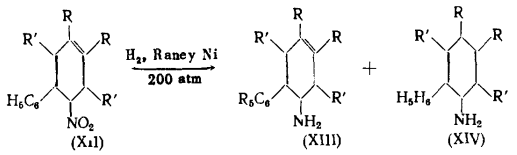
Work on the reduction of the nitro-group in γ-nitro-alkenes does not permit of any general recommendations on the choice of reducing agent.

Parham and coworkers[99] studied the reduction of 3-nitro-2-phenylbicyclo[1,2,2]hept-5-ene by various agents, and they showed that only iron in hydrochloric acid has a selective action:



§ For more details see the next Section.

As the results of the work show, catalytic methods do not permit the selective reduction of the nitro-group in this γ-nitro-alkene. However, Nightingale and Tweedie[100], who studied the hydrogenation of some phenylnitrocyclohexenes on Raney nickel, obtained different results:



(XII) (XIII) (XIV)

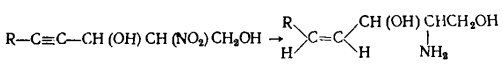
a, R = R′ = H; *b*, R = CH_3, R′ = H; *c*, R = H, R′ = C_6H_5.

The authors found that in (XII, *a–c*), at low temperature and with Raney nickel as catalyst, the nitro-group is first reduced and then the double bond. Thus, at 26° (XII, *a*) gives an almost quantitative yield of (XIII, *a*).

The introduction of methyl groups still further hinders the reduction of the double bond, which in (XII, *b*), for example, cannot be reduced at a temperature below 165°. The introduction of phenyl radicals hinders the reduction of both functional groups; therefore (XII, *c*) is reduced more slowly than (XII, *a*).

The use of other reagents for the selective reduction of (XII, *a–c*) gives less satisfactory results. Thus, when tin(II) chloride and hydrochloric acid in alcohol act on (XII, *a*) the unsaturated amine (XIII, *a*) is formed in 50% yield; however, under the same conditions (XII, *b*) gives a complex mixture of products. The authors also do not recommend zinc in acetic acid of iron(II) sulphate for the selective reduction of the nitro-group in these compounds.

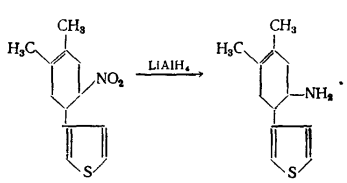
The most effective catalytic method for the selective reduction of unsaturated nitro-compounds uses Lindlar catalyst (palladium on lead carbonate). With the aid of this, Jenny and Druey[35] obtained a series of *cis*-unsaturated aliphatic amines:



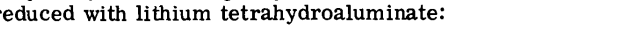
R = n-C_8H_{17}; n-$C_{10}H_{21}$; n-$C_{12}H_{25}$; n-$C_{14}H_{29}$; n-$C_{16}H_{33}$.

When lithium tetrahydroaluminate was used as a reducing agent, the corresponding *trans*-unsaturated amines were obtained.

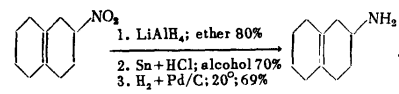
In some γ-nitro-alkenes lithium tetrahydroaluminate reduces only the nitro-group, but in others it reduces both the nitro-group and the double bond. Thus, Nightingale and coworkers[101] described the selective reduction by lithium tetrahydroaluminate of the nitro-group in 1,2-dimethyl-4-nitro-5-thien-3-ylcyclohex-1-ene:



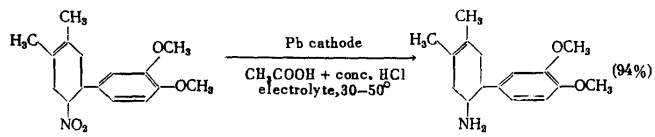
On the other hand, Dornow and Gellrich[34] showed that 3-hydroxy-4-nitro-1-phenylbut-1-ene cannot be selectively reduced with lithium tetrahydroaluminate:



Obviously, the possibility of selectively reducing the nitro-group in γ-nitro-alkenes largely depends on the structure of the initial compound. If the double bond is screened and not activated by other substituents, it is not affected by many reducing agents. For example, Bailev and Golden reduced 2-nitro-9,10-octalin and 2-amino-9,10-octalin by three different methods[102]:



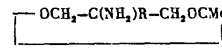
A successful electrochemical method for the selective reduction of γ-nitro-alkenes has been described[103]:



11. Reduction of Nitro-Groups in Compounds with Other Functional Groups

In this section we shall give some examples of the selective reduction of nitro-groups in functional compounds not considered in previous Sections.

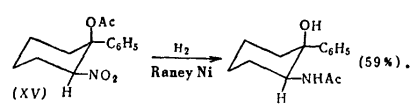
There are two United States patents on the reduction of the nitro-group in nitrodioxans. Morey described a method for the preparation of substituted 5-amino-1,3-dioxans:



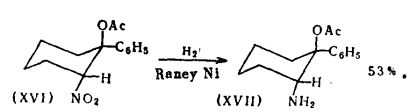
by the catalytic reduction of the corresponding nitro-compounds[104]. The catalyst is not indicated in the patent.

Senkus obtained substituted 5-amino-1,3-dioxans by the catalytic hydrogenation of 5-nitro-1,3-dioxans on Raney nickel at 25° and 130 atm in methanol[105]. The author notes the insecticidal activity of the products obtained.

Interesting information on the reduction of acetates of the stereoisomeric 2-nitro-1-phenylcyclohexan-1-ols and 2-nitro-1-phenylcyclopentan-1-ols is contained in a paper by Bordwell and Garbisch[106]. These workers showed that the reduction of 1-acetoxy-*cis*-2-nitro-1-phenylcyclohexane on Raney nickel is accompanied by transacylation and leads to 2-acetamino-1-hydroxy-1-phenylcyclohexane:

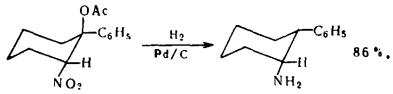


Reduction of the *trans*-isomer proceeds normally:



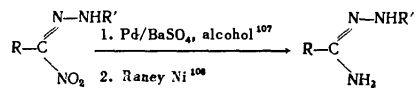
When (XVI) is electrolytically reduced on a platinum cathode at 50°, (XVII) is also formed. Hydrogenation

of (XVI) on palladium is accompanied by elimination of the acetyl group:



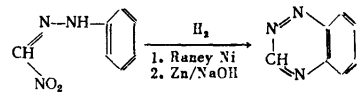
Analogous results were obtained with 1-acetoxy-2--nitro-1-phenylcyclopentenes.

There are hardly any examples in the literature on the selective reduction of aliphatic α-substituted nitro-compounds. Generally, reduction of such compounds proceeds in a complex manner[90]. However, a few instances are known of the selective reduction of hydrazones of alkyl- or aryl-nitroformaldehydes to the corresponding amidrazones[107,108]:



where R = alkyl or aryl.

If R = H and R' = phenyl, the reaction does not stop at the amidrazone stage and leads to triazines[108]:



However, it was not possible to separate the amidrazone as an intermediate product.

Table 3 shows the applicability of various reducing agents to the reduction of the nitro-group in aliphatic nitro--compounds with other functional groups.

Table 3 makes clear the field of application of a given reducing agent for the selective reduction of nitro-compounds; it also shows to what extent the reduction of various classes of nitro-compounds has been studied.

Raney nickel is the most widely used catalyst for the reduction of various nitro-compounds with other functional groups. The reaction is carried out over a wide range of temperature and pressure and, as a rule, in polar solvents (generally alcohols, water, or acetic acid). Other hydrogenation catalysts have not the same general importance; however, of these palladium on lead acetate should be mentioned; hydrogenation on this catalyst does not effect the double bond.

In work with catalysts other than Raney nickel, low pressures and temperatures close to room temperature are used.

Of chemical reducing agents, iron filings and iron(II) salts should be mentioned; with these the reduction usually proceeds in the presence of catalytic quantities of protons:

$$R{-}NO_2 + 3\,Fe + 4\,H_2O \xrightarrow{H^+} R{-}NH_2 + 3\,Fe(OH)_2,$$

or

$$R{-}NO_2 + 2\,Fe + 4\,H_2O \xrightarrow{H^+} R{-}NH_2 + 2\,Fe(OH)_3$$

This permits reduction with iron to be carried out in weakly acid, almost neutral, solution[109].

In spite of the selectivity of tin and tin(II) chloride in hydrochloric acid (they do not attack multiple C–C bonds), they generally give lower yields than catalytic methods and the reduction is sometimes complicated by side-reactions¶.

The use of lithium tetrahydroaluminate, which, as a rule, readily reduces the aliphatic nitro-group to the amino-group, is largely affected by the interaction of this agent with many functional groups (carbonyl, carboxyl, ester, nitrile, triple bond, etc.).

It is of interest to note that when optically active nitro--compounds are reduced with lithium tetrahydroaluminate, optically active amines are obtained[110].

Aluminium amalgam and zinc dust are extremely weak reducing agents. In reduction with zinc in an acid solution, it is sometimes useful to employ copper-coated or amalgamated zinc[111,112].

Until recently the possibility of selectively reducing nitro-groups in aliphatic compounds by such reagents as hydrazine with the addition of platinum or palladium, titanium sulphate[113], NH_4–Hg amalgam[114], etc. was not considered. However, these agents reduce the nitro--group in aromatic nitro-compounds extremely rapidly and easily.

The electrochemical method has also not been sufficiently used for the selective reduction of nitro-groups in polyfunctional aliphatic compounds.

TABLE 3.

Reducing agent for nitro-groups	Functional groups														
	C=C	C≡C	OH	C=O	COOH or COOR	C≡N	C—Cl	C—F	SO_3H	SO_2	—S—	OR	C—NH_2	C(=O)—NH_2	N—NO_2
Raney nickel	±	—	+	—	+	—	±	+	+	+	+	+	+	+	+
Palladium on carbon	+	—	+	+	+										
Palladium on $PbCO_3$	+	—	+			—									
Palladium on $BaSO_4$			+	+	+										
Adams catalyst		—	+	—	+			+				+			+
Colloidal Pt	—		+												
Na amalgam			+		+									+	
Al amalgam	+				+										
Zn dust	—														+
Fe + acid	±		+		+	+			+			+			
Zn + acid	—	+	+		+							+			
Sn or $SnCl_2$ + HCl	±		+	—			+	+				+	+		
Na in boiling alcohol			+												
N_2H_4 with addition of Pt or Pd	+														
Lithium tetrahydroaluminate	±	—	+	—	—		+	+				+			

+ selective reduction.
- non-selective reduction.

III. SELECTIVE REDUCTION OF FUNCTIONAL GROUPS IN NITRO-COMPOUNDS

There is relatively little information in the literature on the selective reduction of functional groups in nitro--compounds. This may be explained by the difficulty of this problem, since the nitro-group is one of the functions most sensitive to reduction, and also by the fact that the object of the majority of workers is to find conditions for the reduction of the nitro-groups in order to synthesise the corresponding amines, oximes, or alkylhydroxylamines.

¶ This applies to a greater extent to aromatic nitro-compounds.

In recent years, in connection with the increasing part played by nitro-compounds in industrial practice and theoretical investigations, the attention of chemists has been more and more attracted to the possibility of synthesising nitro-products (mainly nitroalkanes, nitro-alcohols, and nitro-amines) by the selective reduction of the corresponding polyfunctional compounds.

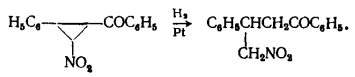
The material in this part of the review is grouped according to general methods of reduction, catalytic, chemical, and electrochemical.

1. Catalytic Reduction of Functional Groups in Nitro--Compounds

Multiple carbon–carbon bonds can usually be easily reduced by catalytic hydrogenation. This obviously explains why most work on the catalytic reduction of polyfunctional nitro-compounds has been done on the reduction of nitro-alkenes.

As early as 1917, work was carried out on the reduction of the double bond conjugated with a nitro-group; this work was done on the nitrostyrenes. Sonn and Schellenberg observed that when nitrostyrenes are hydrogenated on platinum black or colloidal palladium in alcohol at room temperature, selective reduction of the double bond occurs[115]. However, instead of the desired phenylnitroethanes, products formed by the addition of phenylnitroethane to unreduced nitrostyrene were obtained.

Similar results were obtained somewhat later by Kohler and Drake, who showed, moreover, that Kelber nickel cannot be used as a catalyst for the selective reduction of α-nitro-alkenes because the rate of reduction of the nitro--group is similar to the rate of reduction of the double bond[116]. These workers opened the cyclopropane ring of 3-benzoyl-1-nitro-2-phenylcyclopropane without affecting the carbonyl or nitro-group:

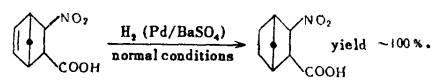


Hurd developed a satisfactory method of selective hydrogenation, not accompanied by dimerisation, for 1-aryl-2--nitroalk-1-enes[117]. He carried out the reduction at 15–40° on platinum or palladium in water, alcohols, ketones or aromatic hydrocarbons and obtained the corresponding 1-aryl-2-nitroalkanes in 25–60% yield. The author noted ketones or oximes as possible secondary products.

It is much easier to reduce a double bond not conjugated with a nitro-group. For this it is expedient to use platinum dioxide in acetic acid at room temperature. Examples are known of the successful selective reduction of the C=C bond with the aid of this catalyst in nitro-alkenes[118], phenylnitrocyclohexenes[119,120] nitronorbornylenes[121] and other nitro-cyclenes of the terpene series[122]. Raney nickel is less suitable for the selective hydrogenation of the double bond, since in a number of instances the double bond is reduced on this catalyst only after reduction of the nitro--group[100].

It should be mentioned that the structure of the nitro--compound undergoing reduction frequently affects the nature of the products of catalytic hydrogenation. Thus, Young and Snyder succeeded in hydrogenating the phenyl ring of ethyl 3-(2-nitrobutyl)indole-2-carboxylate without affecting the nitro- or the ester group[123]. The catalyst was 30% palladium on charcoal, and the reaction was carried out at room temperature under a hydrogen pressure of 3 atm in acetic acid. The authors consider that the course of this reaction is explained by a combination of steric and electronic factors that protect the nitro-group in this compound. It is also known that the double bond conjugated with the nitro-group can be selectively reduced in 1,2-dideoxy-1-nitro-D-*arabo*-hexitoltetraacetate, the molecule of which contains several ester groups[124]; the reaction was carried out on palladium black in absolute alcohol under normal conditions.

Recently Yur'ev and coworkers[125] described the selective reduction of 2-nitro-3,6-*endoxo*-Δ^4-tetrahydrobenzoic acid in acetone with palladium on barium sulphate:



There are no references whatever in the literature on the possibility of the catalytic selective reduction of carbonyl-containing functional groups in aliphatic nitro-compounds.

On the contrary, as is shown in Section II, in a number of instances the nitro-group is first reduced[44]. Catalytic reduction of the sulpho-group is also impossible in the presence of a nitro-group[88].

The examples given therefore exhaust all information on the catalytic selective reduction of functional groups in aliphatic nitro-compounds. It is clearly obvious that this method is not general, and in effect can only be used for the reduction of multiple bonds in nitro-alkenes; even here the reaction is sometimes complicated by the formation of secondary products. It should also be noted that the catalytic hydrogenation of functional groups in polynitro-compounds is not described in the literature, and it may be supposed that this would be a still more complicated process.

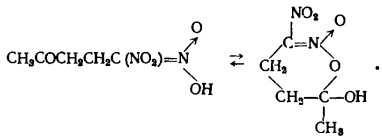
2. Chemical Reduction of Functional Groups in Nitro--Compounds

As is shown in Section II, reduction by atomic hydrogen, obtained by the interaction of metals with acids and alkali metals with alcohols, is one of the most widely used methods for the chemical reduction of the nitro-group and cannot be used for the selective reduction of functional groups in nitro-compounds. In the same way, chlorides of metals of variable valency which react with the nitro--group must also be excluded.

In the past decade the method of chemical reduction with complex hydrides of the alkali and alkaline earth elements has been widely developed. This method was very promising for the selective reduction of functional groups in nitro--compounds, because of the relative stability of nitro--groups to hydride anions. Moreover, at present there is a great selection of hydride reducing agents with the most diverse sensitivity to a number of functional groups.

Shechter[126] showed that nitro-ketones and nitro-aldehydes may be reduced in good yield to nitro-alcohols with sodium tetrahydroborate in aqueous-methanolic solution at pH 3–10.5. and a temperature from 0° to 25°. 1,1-Dinitropentan-4-one formed an exception; even with a considerable excess of reducing agent this gave a low yield of

nitro-alcohol. The author explains this by the existence of the initial compound as an equilibrium mixture:



Shechter suggests that sodium tetrahydroborate is particularly useful for the selective reduction of the most labile nitro-ketones and nitro-aldehydes. He also recommends the reduction of the carbonyl group in more stable nitro-ketones and nitro-aldehydes by aluminium isopropoxide† in isopropyl alcohol or toluene (for more "acid compounds"); aldehydes are reduced more rapidly than ketones, and the yields of nitro-alcohols are connected in the following manner with the nature of the nitro-group in the initial compounds:

$$t\text{-}NO_2 > s\text{-}NO_2 > primary\text{-}NO_2.$$

It is known that at room temperature lithium tetrahydroaluminate reduces the nitro-group in nitro- [36,58] and polynitro-compounds [42]. However, it has beenshown by Feuer and Kucera [129] that in ether at -30° and -60° this is a stronger reducing agent than sodium tetrahydroborate and may be used for the selective reduction of esters containing secondary and tertiary nitro-groups and even *gem*--dinitro-groups. The yields of nitro-alcohols are 53–76%. Hence, Shechter [126] and Feuer [129] have developed a new method of obtaining nitro-alcohols, greatly extending the range of these compounds, which are of practical interest.

In 1963, Gold and Klager published a paper on the reduction with sodium tetrahydroborate of the chlorides of a number of nitro-acids, including trinitrobutyric acid [130]; the corresponding nitro-alcohols were always obtained (see Table 4).

The authors also describe the reduction of some ketones containing $C(NO_2)_3$ groups, but they do not give yields, constants of the alcohols obtained, or experimental methods:

$$C(NO_2)_3CH_2CH_2COCH_3 \xrightarrow{NaBH_4} C(NO_2)_3CH_2CH_2CH(OH)CH_3,$$

$$C(NO_2)_3CH_2CH_2COCH_2OH \xrightarrow{NaBH_4} C(NO_2)_3CH_2CH_2CH(OH)CH_2OH.$$

TABLE 4.

Initial acid chloride	Alcohol obtained	Yield, %
$CH_3—C(NO_2)_2(CH_2)_2COCl$	$CH_3C(NO_2)_2(CH_2)_3CH_2OH$	63
$CH_3—C(CH_3)NO_2(CH_2)_2COCl$	$CH_3C(CH_3)NO_2(CH_2)_2CH_2OH$	70
$C(NO_2)_3(CH_2)_2COCl$	$C(NO_2)_3CH_2CH_2CH_2OH$	65
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2COCl$	$CH_3C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$	82
$(NO_2)_2C(CH_2CH_2COCl)_2$	$(NO_2)_2C(CH_2CH_2CH_2OH)_2$	50
$(NO_2)_2C[CH_2C(NO_2)_2CH_2CH_2COCl]_2$	$(NO_2)_2C[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	63
$(NO_2)HC[CH_2C(NO_2)_2CH_2CH_2COCl]_2$	$NO_2CH[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	85
$N(NO_2)—[CH_2C(NO_2)_2CH_2CH_2COCl]_2$	$N(NO_2)[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	85

† It should be mentioned that isolated instances of selective reduction of the carbonyl group in nitrocyclopropyl ketones had previously been known [127,128]. However, the authors of these papers did not aim at developing a general method of preparing nitro--alcohols.

Recently, a number of patents appeared on the preparation of the latter polynitrodiol from hydroxymethyl 3,3,3--trinitropropyl ketone with the aid of sodium tetrahydroborate. [131-134] The authors point out that this diol may be used as an intermediate in the synthesis of components of solid rocket propellents.

Ioffe and coworkers [135] showed that a solution of diborane in tetrahydrofuran (THF) may be used for the reduction of aliphatic mononitro-acids:

$$CH_2NO_2CH_2COOH + B_2H_6 \xrightarrow{THF} (NO_2)CH_2CH_2CH_2OH.$$

Diborane in tetrahydrofuran is also suitable for the reduction of esters of nitro-acids, but the presence of such electronegative substituents as nitro-groups sharply reduces the rate of reduction of the ester group.

Alkali metal tetrahydroborates (for example, sodium tetrahydroborate or sodium hydrotrimethoxyborate), which are reducing agents of the nucleophilic type, may be used very successfully also for the preparation of nitroalkanes and conjugated nitroalkenes [136], since the influence of the nitro-group ensures the possibility of nucleophilic attack of the BH_4^- and $BH(OCH_3)_3^-$ anions on the double bond. According to Shechter, the reduction mechanism includes nucleophilic attack of the relatively positive carbon atom of the C=C group of the conjugated nitro-alkene. Evidently, the initially formed metal trihydro(monoalkanenitronato)-borate Li or $Na(R_2CHCR'{=}NO_2)BH_3$ enters into further reactions giving a metal tetrakis(alkylnitronato)borate which is converted into the nitroalkane after hydrolysis. The course of the reactions may be represented by the following equations:

$$R_2C{=}CR'NO_2 + NaBH(OCH_3)_3 \rightarrow R_2CHCR'NO_2Na + B(OCH_3)_3,$$

or

$$4R_2C{=}CR'NO_2 + BH_4^- \xrightarrow[Na^+]{Li^+} [(R_2CHCR'{=}NO_2)_4B]^-.$$

The yield of nitroalkanes is 50–80%. The introduction of electronegative substituents, which increase the electron deficiency of the double bond, accelerates reduction. For this reason, the reaction with sodium and lithium tetrahydroborates is suitable for the selective reduction of conjugated fluoronitroalkenes (for example, 4,4,5,5,6,6,6-heptofluoro-2-nitrohex-2-ene). The reduction of nitroalkenes is usefully carried out at the lowest possible temperatures (-50°, -70°); the alkene is added to the metal tetrahydroborate to reduce the dimerisation side reaction:

$$R_2CHCR'{=}NO_2^- + R_2C{=}CR'NO_2 \rightarrow R_2CHCR'(NO_2)CR_2CR'{=}NO_2^-.$$

The reduction of sterically hindered nitroalkenes (for example, 3-nitrohept-4-ene) cannot be fully effected even at 0°. The reaction with such alkenes is carried out at room temperature.

The C=C bond in conjugated nitroalkenes may be reduced in the presence of ester groups by means of alkali tetrahydroborates [136]. In particular, the double bond in 1,2-dideoxy-1-nitro-D-*arabo*hexitol tetraacetate has been reduced with sodium tetrahydroborate [136]; the yield of product was 55–65% (for the catalytic reduction see Sowden and Fischer [124].) It has also been observed that, because of the strong inductive effect, closely situated nitro-groups activate ester groups to such an extent that they are reduced by metal tetrahydroborates [136]. Both sodium tetrahydroborate and sodium hydrotrimethoxyborate successfully reduce 2-nitrobutyl acetate at 3–5° to the corresponding alcohol, although generally under these conditions these reagents do not affect the ester gruup.

Cook and coworkers[83] showed that α-nitro-alkenes (including those containing fluorine) may be reduced to fluoronitro-alkanes in 35–55% yield by the action of lithium tetrahydroaluminate in anhydrous ether at -50°. Shechter and coworkers, who studied this reaction, also observed that it proceeds smoothly at temperatures below -40° after addition of lithium tetrahydroaluminate to the alkene undergoing reduction[136]. If the reagents are mixed in a different order, polymerisation occurs.

There are some very interesting results on the chemical reduction of the halogen in α-halogenonitro-compounds. In 1893, Duden showed that dibromodinitromethane is reduced to dinitromethane in 70–80% yield by the action of arsenic trioxide in potassium hydroxide solution[137]. Similar results are obtained by treatment of dibromodinitromethane with aqueous ammonia solution of hydrogen sulphide. Somewhat later, Pratt observed that the halogen in nitromethane derivatives can be reduced by an alkaline solution of hydrazine[138]‡:

$$CX(NO_2)_3 + NH_2{-}NH_2 \xrightarrow{KOH} CH(NO_2)_3,$$

$$RCHBrNO_2 + NH_4{-}NH_2 \xrightarrow{KOH} RCH_2NO_2,$$

$$CBr_2(NO_2)_2 + NH_2{-}NH_2 \xrightarrow{KOH} CHBr(NO_2)_2,$$

$$CCl_3NO_2 + NH_2{-}NH_2 \xrightarrow{KOH} CCl_2H(NO_2),$$

where X = Cl or Br, R = H or C_6H_5.

Iffland proposed the reduction of α-bromonitro-compounds of the aliphatic and alicyclic series to the corresponding nitro-alkanes (yield 15–80%) by sodium tetrahydroborate in aqueous methanol solution[139,140]. Although ordinary halogenoalkanes are inert to sodium tetrahydroborate, the reduction of α-bromonitro-compounds becomes possible, evidently because of the strong inductive effect of the nitro-groups, which facilitates nucleophilic attack of the tetrahydroborate anion on the carbon atom carrying the halogen and the nitro-group. As a result of his investigations, Iffland[139,140] proposed a new method of preparing nitroalkanes from the corresponding carbonyl compounds:

$$R_2C{=}O \rightarrow R_2C{=}NOH \xrightarrow{\text{bromosuccinimide}} \left[\begin{array}{c} Br \\ | \\ R_2{-}C{-}N{=}O \end{array}\right] \rightarrow$$

$$\rightarrow R_2CBrNO_2 \xrightarrow{NaBH_4} R_2CHNO_2.$$

Klager has described the reduction of αα-tetrabromodinitro-compounds by sodium tetrahydroborate[141]:

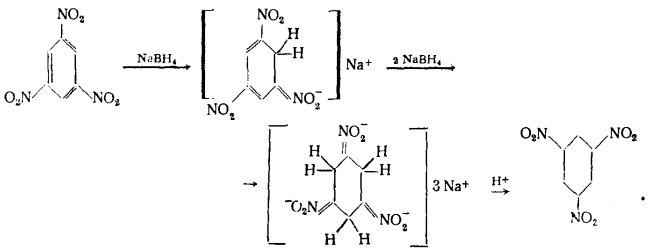
$$CBr_2NO_2CH_2CH_2CBr_2NO_2 \xrightarrow{NaBH_4} CH_2NO_2CH_2CH_2CH_2NO_2.$$

Thus, α-halogenonitro-alkanes may be reduced in several ways to nitro-alkanes. However, as has been shown in Section II.7, only the nitro-group is usually reduced in other halogenonitro-compounds.

Although the present review is concerned with aliphatic nitro-compounds, the work of Severin and Schmitz should be briefly mentioned[142-147]; they showed that the aromatic ring in polynitrobenzenes could be selectively reduced with sodium tetrahydroborate.

‡ It is interesting to note that aromatic nitro-groups, in contrast to aliphatic, are readily reduced by hydrazine.

The alkali tetrahydroborates are, as a rule, inert to aromatic systems, but because of the strong electron-acceptor activity of the nitro-groups, BH_4^- can attack the carbon atoms of the ring, for example:



More detailed information on this question is given in the literature[142-147].

It can be concluded from the material discussed here that the use of complex metal hydrides has substantially extended the possibility of selectively reducing functional groups in nitro-compounds; in particular it has, for the first time, permitted the preparation of a large number of nitro-alcohols from the corresponding carbonyl-containing compounds.

3. Electrochemical Reduction of Functional Groups in Nitro-Compounds

The only work on the selective reduction of functional groups in aliphatic nitro-compounds by an electrochemical method is that of Mairanovskii and coworkers[148], who investigated α-halogenonitroalkanes. These workers found that the effect of the nitro-groups facilitates the polarographic reduction of the C–Hal bond, and the wave corresponding to this process precedes the wave corresponding to the reduction of the nitro-group. This order of the waves was observed for mononitro-, dinitro-, and trinitro-alkanes containing chlorine, bromine, or iodine in the α-position to the nitro-groups.

There is some indirect information indicating the possibility of selectively reducing the carbonyl group in nitro-compounds by an electrochemical method. Shikata and Tacho established that the reduction potentials of ketones, azo-, and nitro-compounds are proportional to the electronegativity of the substituents linked to the group undergoing reduction[149]. Obviously, it should be possible to select substituents such that their carbonyl group is reduced by an electrochemical method before the nitro-group. However, there is no information on this question in the literature

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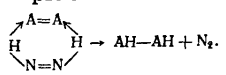
In conclusion, some hydrogenation catalysts will be briefly discussed that do not reduce the nitro-group, and also reagents that weakly react (or do not react at all) with the nitro-group, but are capable of reducing some functional groups. However, these have not yet been used for the selective reduction of polyfunctional nitro-compounds.

According to Japanese workers, the hydrogenation of 1-nitropropane on a catalyst of metal formates (for example, Ni and Zn, or Zr and V formates) is difficult[150].

A silk–palladium catalyst, generally used for the hydrogenation of multiple bonds in alkenes, aldehydes and nitriles, has similar properties[151].

Broadbent and Johnson[152] recently described a catalyst based on rhenium oxide ($Re_2O_7.3C_4H_8O$) with a wide spectrum of activity. It can be used for readily hydrogenating aromatic systems, but it also reduces carbonyl and carboxyl groups to alcohols groups, and nitriles to amines; this catalyst is inert to aliphatic nitro-compounds (for example, 2-nitropropane) and reduces aromatic nitro-compounds (for example, nitrobenzene) with difficulty. However, m-nitroacetophenone is very inert to its action, and, thus, the introduction of the nitro-group may render the carbonyl group and the atomatic nucleus passive.

Diimide readily reduces symmetrical multiple bonds (C=C, C≡C, N=N, O=O, etc.) with which it apparently forms a transition complex[153,154]:



→ AH—AH + N_2.

However, the formation of such a complex with two unlike charged atoms is difficult, and therefore the reduction of groups of the type C=N, NO_2, C≡N, S=O, and C=O proceeds much more slowly. In particular, nitroethane is comparatively stable to the action of azodiimide[153].

It should be noted that some nitro-compounds are not affected by calcium hydride[155].

Some neutral complexes of borine and alkylborines that do not react with the nitro-group should also be mentioned[156]; these have hardly been used for the reduction of polyfunctional aliphatic nitro-compounds.

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POLYMER SYNTHESIS BY CYCLIC POLYMERISATION

S.G. Matsoyan

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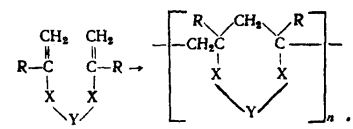
I. INTRODUCTION

In connection with studies on the synthesis of polymers with valuable technical properties, in particular high thermal stability, there has been a considerable increase of interest in recent years in polymeric compounds containing cyclic groupings in the main chain [1-3]. At the present time extensive experimental data have been accumulated on the synthesis of various cyclic polymers, their structure, and their properties.

When the information available in the literature is generalised and systematised, it becomes clear that introduction of cyclic groupings, carbocyclic and heterocyclic units, into the main polymer chain can be achieved in three principal ways: by cyclic polymerisation, polycondensation, and chemical modification of polymeric compounds. Cyclic polymerisation can in turn be subdivided into two classes according to the mode of formation of the rings: chain polymerisation and stepwise polymerisation. The latter class includes polymerisation by the Diels-Alder reaction [4], thermal polymerisation of allene hydrocarbons [5], and others.

In the present review only cyclic polymers obtained by cyclic chain polymerisation are considered. In the field of cyclic polymerisation the so called intermolecular-intramolecular polymerisation of non-conjugated dienes has at present undergone the greatest development [6]. This type of cyclic polymerisation was discovered as a result of studies by several investigators [7-11], in particular Butler and coworkers [12,13]. It consists essentially in intramolecular ring closure of non-conjugated dienes, in particular 1,6-dienes, with simultaneous intermolecular chain growth, according to the following general mechanism:

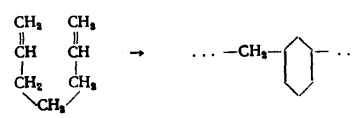


The polymerisation of other unsaturated systems, cyclodiene, triene, and vinylacetylene compounds and bifunctional compounds (dialdehydes, diepoxides) has also been investigated, using all known methods of initiation, with the aim of synthesising cyclic polymers. It was established that cyclic units in the polymer chain can form by intramolecular cyclisation of the monomer and interaction of two or several monomeric units of various types. For this reason, we shall give the name cyclic polymerisation to any type of polymerisation which leads to the introduction into the main polymer chain of cyclic groupings, regardless of the structure and nature of the monomer.

II. SYNTHESIS OF CARBOCYCLIC POLYMERS

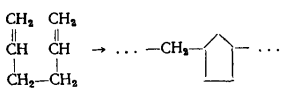
1. Polymerisation of Non-Conjugated Dienes.

A. Polymerisation of diene hydrocarbons. Marvel and Stille [14] were the first to show the possibility of the cyclic polymerisation of non-conjugated diolefins under the influence of complex metal alkyl catalysts. A solid, benzene-soluble polymer with cyclohexane rings in the chain, melting at 210-230° and having an intrinsic viscosity $[\eta] = 0.2-0.4$, was obtained from hepta-1,6-diene under the action of the $Al(iso\text{-}C_4H_9)_3$-$TiCl_4$ catalytic system:



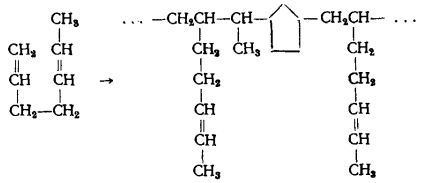
Rigid rubberlike polymers, the degree of cyclisation in the soluble fraction of which reaches 87%, are obtained under similar conditions from hexa-1,5-diene and 2,5-dimethylhexa-1,5-diene. Recently Makowski et al. [15] obtained in

the presence of aluminium triethyl and titanium tetrachloride a crystalline polyhexa-1,5-diene consisting of 1-methylene-3-cyclopentyl units:

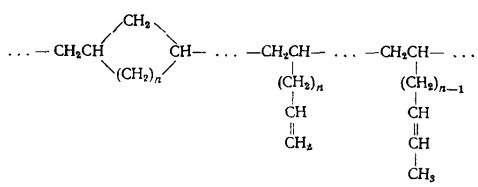


Its melting range extended to 146° and its intrinsic viscosity $[\eta]$ ranged up to 2.

The thermal stability of the cyclic polymers of hexa--1,5-diene, 2-methylhexa-1,5-diene, and hepta-1,6-diene was investigated by Anderson [16]. In the polymerisation of hepta-1,5-diene in the presence of aluminium triethyl and titanium tetrachloride a transparent rubberlike soluble product, consisting on average of 13 monomer units, was obtained [17]. It was established that the polymer contains units of two types in proportions of about 1 : 2: five--membered rings and branched groups with an internal double bond.



Marvel and Garrison [18] synthesised and studied the cyclic polymerisation of di-olefinic hydrocarbons with a long chain in the presence of Ziegler type catalysts. The degree of cyclisation of the soluble fraction of the polymers depends on the size of the rings formed (Table). The authors represent the structure of these polymers in the following way:

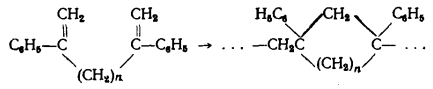


Field [19] studied the thermal polymerisation of 2,6-diphenylhepta-1,6-diene in the presence of free-radical initiators and anionic and cationic catalysts. According to his data, the polymerisation proceeds by a cyclic mechanism regardless of the method of initiation and leads to the formation of a polymer with six-membered rings in the chain. Using the method developed by Field, Marvel and Gall [20,21]

TABLE. Degree of cyclic polymerisation of di-olefins.

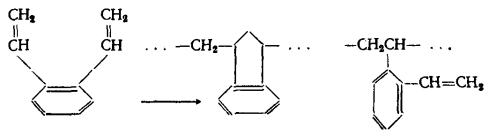
n in $CH_2=CH\diagdown\diagup(CH_2)_n$	Number of ring atoms	% of cyclic units in the soluble fraction of polymers	n in $CH_2=CH\diagdown\diagup(CH_2)_n$	Number of ring atoms	% of cyclic units in the soluble fraction of polymers
4	7	25	9	12	11
5	8	9	11	14	15
6	9	6	12	15	15
7	10	10	14	17	4
8	11	11	18	21	8

synthesised several phenyl-substituted diene hydrocarbons and studied their capacity for cyclic polymerisation:

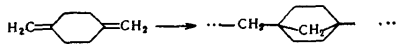


where n = 2, 3, 4.

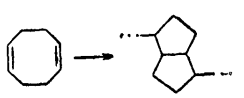
In the radical polymerisation of *o*-divinylbenzene [22] in benzene solution a soluble polymer (melting at 400° with decomposition) whose degree of cyclisation varied markedly with the reaction temperature and monomer concentration, was obtained. A kinetic equation for the calculation of the proportions of cyclic and vinyl polymerisation was derived.



Many investigators used cyclic polymerisation to prepare polymers with bicyclic bridge units. Ball and Harwood [23] obtained from 1,4-dimethylenecyclohexane under the action of gaseous boron trifluoride a soluble polymer (yield 85%, $[\eta]$ = 0.07) which does not melt up to 250°. The repeating unit in this polymer is methylene-1,4-bicyclo-[2,2,1]heptane:

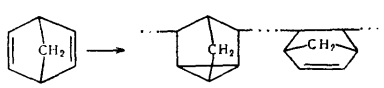


In the polymerisation of *cis,cis*-cyclo-octa-1,5-diene [24] under the action of the Ziegler catalyst a polymer (m.p. 100–180°, $[\eta]$ = 0.02–0.04) with a unit structure similar to bicyclo[3,3,0]octane was obtained:

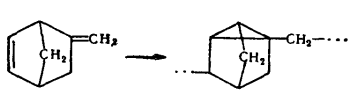


In the attempted preparation of a bridge-type polymer from cyclohexa-1,4-diene under similar conditions only rearrangement with formation of polycyclohexa-1,3-diene was observed.

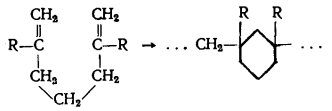
According to Zutty's data [25], in the presence of a free--radical initiator bicyclo[2,2,1]hepta-2,5-diene is converted into a low-molecular-weight soluble polymer containing both 3,5-disubstituted nortricyclene units and 5,6-disubstituted bicyclo[2,2,1]hept-2-ene units in the chain:



Bridge polymerisation [26] of 2-methylenenorborn-5-ene in the presence of aluminium tribromide leads to the formation of a polymer (m.p. 150–160°, $[\eta]$ = 0.3) whose units are produced by opening of both double bonds in the monomer with simultaneous formation of a bridge bond:

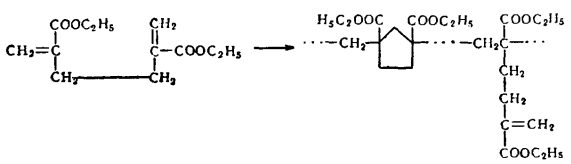


B. Polymerisation of substituted hepta--1,6-dienes, hexa-1,5-dienes, and penta--1,4-dienes. Marvel and Vest[27,28] studied the cyclic polymerisation of $\alpha\alpha'$-dimethylenepimelic acid and its methyl and ethyl esters, nitrile, and amide in the bulk, in solution, and in emulsion; in most cases soluble polymers were obtained, melting in the range 125–300° and having $[\eta] = 0.14–0.73$:

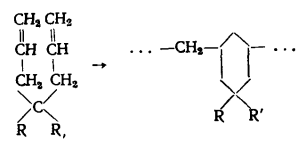


where R = COOH, $COOCH_3$, $COOC_2H_5$, CN, and $CONH_2$.

With the aim of synthesising soluble polymers having a high molecular weight, Milford[29] made a detailed study of the conditions of the cyclic polymerisation of the methyl ester and nitrile of $\alpha\alpha'$-dimethylenepimelic acid; on ultraviolet irradiation in solution in tetramethylenesulphone at 20° in the presence of benzoin as the photo-initiator, the corresponding cyclic polymers were obtained in 74–80% yield with $[\eta] = 2.03$ and 1.2 respectively. Radical polymerisation of 2,5-dicarbethoxyhexa-1,5-diene[28] in benzene solution leads to the formation of a cyclic polymer (m.p. 110–120°, $[\eta] = 0.21$) containing up to 10% of open-chain units:

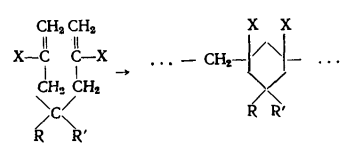


Matsoyan and his coworkers[30-32] studied the capacity for cyclic polymerisation of a number of 4-substituted hepta-1,6-dienes in the presence of radical initiators. The cyclic structure of the polymers obtained was demonstrated by chemical and spectroscopic methods:



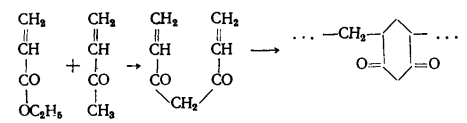
where R = H, R′ = COOH, $COOC_2H_5$, $COOC_6H_5$, $CONH_2$, $CON(CH_3)_2$, $CONHC_6H_5$, $COCH_3$, OH, $OCOCH_3$, $OCOC_6H_5$, Cl, CN; R = R′ = $COCH_3$; R = R′ = $COOC_2H_5$; R = $COCH_3$, R′ = $COOC_2H_5$; R = COOH, R′ = CN; R = $COOC_2H_5$, R′ = = CN.

These workers investigated the effect of the nature of the substituents (in positions 2, 4, and 6) on the cyclic polymerisation of substituted hepta-1,6-dienes[30-33]; the presence of methyl groups in positions 2 and 6 retards cyclic polymerisation while the presence of chlorine atoms sharply accelerates it. Under conditions of cyclic polymerisation 2,6-dichloro-4-substituted hepta-1,6-dienes undergo up to 70% dehydrochlorination:



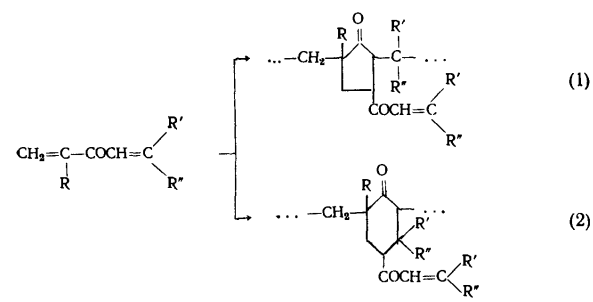
where X = CH_3 and R = R′ = $COOC_2H_5$; R = H, R′ = CN; R = $COOC_2H_5$, R′ = CN; R = COOH, R′ = CN; or X = Cl and R = R′ = $COOC_2H_5$; R = H, R′ = COOH; R = $COCH_3$, R′ = $COOC_2H_5$.

The mechanism of the cyclic polymerisation of some of the 4-substituted hepta-1,6-dienes described above was also studied by other investigators[34,35]. Jones[36] showed that in the Claisen condensation of ethyl acrylate with methyl vinyl ketone in the presence of sodium methoxide, a soluble coloured polymer (M = 2000) melting at 190° is formed instead of the expected diacryloylmethane. The author suggests that the actual product is a cyclic polymer of diacryloylmethane:



Somewhat later[37] in a detailed study of the condensation product described by Jones it was found that it is a copolymer of methyl vinyl ketone and diacryloylmethane. Bloomfield[38] synthesised the monomeric diacryloylmethane by the pyrolysis of the diene reaction adduct[39] and found that under the conditions used by Jones diacryloylmethane forms an insoluble three-dimensional polymer. However, later Marvel and coworkers[40] succeeded in obtaining in the presence of sodium methoxide at -75° a cyclic homopolymer of diacryloylmethane as a light yellow powder soluble in dimethylformamide.

Matsoyan and coworkers[41-43] showed that radical polymerisation of 1,4-dienes, substituted divinyl ketones, leads to the formation of solid soluble polymers containing cyclopentane or cyclohexane rings, depending on the structure of the monomers, instead of the expected four-membered rings; the polymer unit is formed by the cyclisation of two monomer molecules. The polymerisation of β-methylvinyl, di-(β-methylvinyl), β-t-butylvinyl, β-methylvinyl, α-methylvinyl β-methylvinyl, and ββ-dimethylvinyl α-methylvinyl ketones proceeds according to reaction (1), while dienes containing allyl groupings of the type $-COCH=CR-CH_2-$, β-ethylvinyl vinyl, β-n-propylvinyl vinyl, β-ethylvinyl β-methylvinyl, di-(β-ethylvinyl), and ββ-pentamethylene-vinyl vinyl ketones form polymers according to reaction (2):



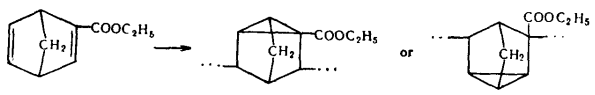
(1)

(2)

Arbuzova and Mosevich[44] obtained a soluble polymer ($[\eta] = 0.054$) with a cyclopentane ring in the chain by prolonged heating of dibenzylideneacetone at 130° in the presence of benzoyl peroxide.

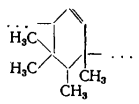
Radical polymerisation of 2-ethoxycarbonylbicyclo-[2,2,1]hepta-2,5-diene[45] yielded a soluble saturated polymer

with a vitrification temperature of 220° ([η] = 1.32–1.92). The principal structural units of this polymer are nortricyclenes:



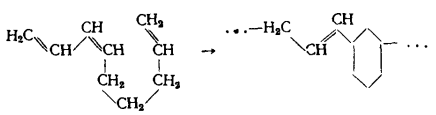
2. Polymerisation of Unsaturated Compounds of Other Types

Following the publication of studies on the cyclic polymerisation of non-conjugated dienes, reports appeared on the synthesis of carbocyclic polymers from unsaturated compounds of other types. Jones [46] studied the structure of soluble polymers of 2,6-dimethylocta-2,4,6-triene (allo-ocimene), whose polymerisation in the presence of cationic catalysts [47] has been known for a long time. On the basis of the data obtained and the known fact of the ease of cyclisation of allo-ocimene into α- and β-pyronenes [48,49], Jones suggested the following cyclic structure for polyallo-ocimene:

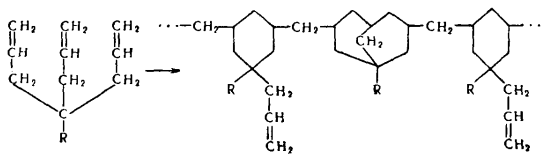


Marvel and coworkers [50,51] polymerised allo-ocimene under the action of anionic and cationic catalysts and made a detailed study of the structure of the polymers obtained. They found that the polymerisation of allo-ocimene proceeds mainly according to the usual linear mechanism, the degree of cyclisation being slight.

Butler and Brooks [52,53] showed that the polymerisation of triene hydrocarbons, *trans*-nona-1,3,8-triene, *cis*-nona-1,3,8-triene, and octa-1,3,7-triene, under the influence of aluminium triethyl and titanium tetrachloride leads to the formation of cyclic polymers as a result of simultaneous 1,2 and 1,4 intramolecular addition and chain growth:

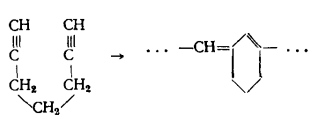


Matsoyan et al.[54] showed that, on radical polymerisation of branched trivinyl compounds such as triallylmethane derivatives, there is both monocyclic and bicyclic chain growth in proportions of 1 : 2:

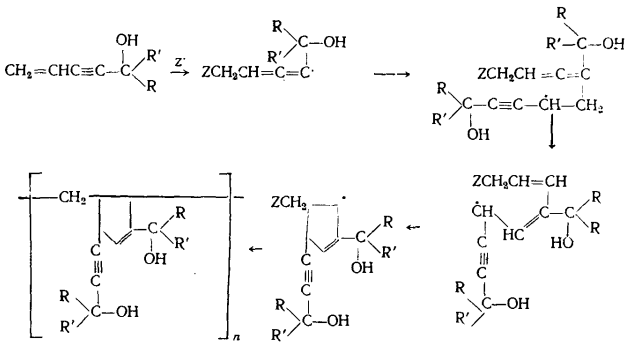


where R = OH, $OCOCH_3$, CN, $CONH_2$.

Stille and Frey [55] applied the cyclic diene polymerisation to hepta-1,6-diyne, octa-1,7-diyne, and nona-1,8-diyne. The polymers obtained in the presence of the Ziegler catalyst were brown or black in colour, which is probably due to double bond conjugation in the polymer chain:



Despite the view expressed in the literature [56], Matsoyan and coworkers [57–60] showed that the polymerisation of ethynylvinyl carbinols, both spontaneous and initiated, proceeds according to a chain mechanism and leads to the formation of high-molecular-weight soluble linear polymers, which are not cross-linked and are completely stable even on heating. According to the mechanism proposed [61,62], cyclic polymerisation of vinylacetylenic alcohols occurs as follows:



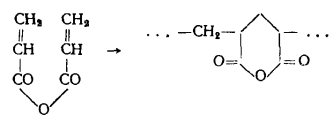
where R and R′ are aliphatic, alicyclic, aromatic and heterocyclic residues.

The kinetics of the cyclic polymerisation of ethynylvinyl carbinols have been studied [63,64]. Carbocyclic polymers of similar structure were obtained from ether derivatives of ethynylvinyl carbinols [65,66]. The possibility of the formation of linear-cyclic polymers from alicyclic [67] and aromatic [68,69] ethynylvinyl carbinol and also certain other vinylacetylenic compounds [70,71] has likewise been demonstrated. The dielectric properties of the cyclic polymer of dimethylvinylethynyl carbonil were studied by Kocharyan et al.[72]

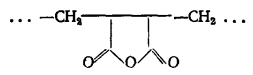
III. SYNTHESIS OF HETEROCYCLIC POLYMERS

1. Polymerisation of Non-Conjugated Systems Containing a Hetero-Atom

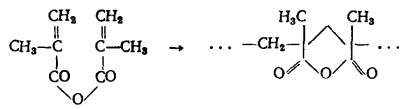
A. Polymerisation of oxygen-containing dienes. The formation of oxygen-containing heterocyclic polymers was first observed by Simpson and coworkers [7,9] in a study of the polymerisation of diallyl carbonate, oxalate, malonate, succinate, phthalate, glutarate, isophthalate, adipate, azelate, and sebacate, and also dimethylallyl carbonate and phthalate. It was found that the capacity of these esters for cyclisation does not always depend on the size of the ring formed (from eight- to seventeen-membered), although it might have been expected that the degree of cyclisation would decrease as the distance between the two allyl groups of the monomer increases. In order to obtain six-membered oxygen-containing heterocyclic polymers, Crawshaw and Butler [73] investigated almost simultaneously with Jones [74] the polymerisation of acrylic anhydride in the bulk and in solution using radical initiators and polymerisation regulators. The authors found that the chain units of the soluble polymers obtained consist of the anhydride of 5-methyleneglutaric acid:



Later Mercier and Smets [75,76] studied the kinetics of the cyclic polymerisation of acrylic anhydride and the structure of the polymer formed as a function of reaction temperature. At 115° and above the polymerisation leads to the formation of five-membered anhydride units in the chain:



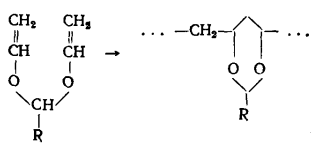
A cyclic polymer of methacrylic anhydride (m.p. 200°, $[\eta]$ = = 0.6–0.8) was obtained by Bresler et al.[77] in the radical polymerisation of the monomer in dimethylformamide:



The same polymer was synthesised by the authors by thermal dehydration of polymethacrylic acid.

In a study of the kinetics of the cyclic polymerisation of methacrylic anhydride Gibbs and Murray[78] found that the effective activation energy for the process is 23 kcal mole^{-1}. In order to confirm that the polymerisation of acrylic and methacrylic anhydrides proceeds accordingly to an intermolecular-intramolecular mechanism, Miyake[79] made a detailed study of the infrared spectra of the polymers. The stereochemical configuration of the cyclic polymers of the anhydrides of the unsaturated acids was determined[80–82]; it was shown by nuclear magnetic resonance that the poly(methyl methacrylate) obtained from the cyclopolymer of methacrylic anhydride has a stereoregular structure.

Matsoyan and Avetyan[83,84] demonstrated the possibility of obtaining acetals of poly(vinyl alcohol) directly from the monomers by the cyclic polymerisation of divinyl acetals. Later this reaction was used to prepare a wide variety of aliphatic[85–90], aromatic, and heterocyclic[91–95] poly(vinyl acetals):

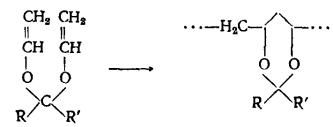


where R = H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, iso-C_4H_9, C_5H_{11}, C_6H_{13}, $CH_3O(CH_2)_2$, $C_2H_5O(CH_2)_2$, $C_3H_7O(CH_2)_2$, $ClCH_2CH_2O(CH_2)_2$, C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 2,4-$(CH_3)_2C_6H_3$, 2,5-$(CH_3)_2C_6H_3$, 3,4-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3$-C_6H_2, 2-$CH_3OC_6H_4$, 3-$CH_3OC_6H_4$, 4-$CH_3OC_6H_4$, 2-$C_2H_5OC_6H_4$, 2-$C_3H_7OC_6H_4$, 2-iso-$C_3H_7OC_6H_4$, 2-$C_4H_9OC_6H_4$, 2-iso-C_4H_9-OC_6H_4, 2-$C_5H_{11}OC_6H_4$, 2-iso-$C_5H_{11}OC_6H_4$, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, α-$C_{10}H_7$, α-C_4H_3O.

The polymerisation of divinyl acetals occurs in the bulk and in solution in the presence of radical iniators and under the influence of ionic catalysts. It was found that in the cyclic polymerisation the steric configuration and the presence of an axis of symmetry in the monomeric divinyl acetal molecules are important.

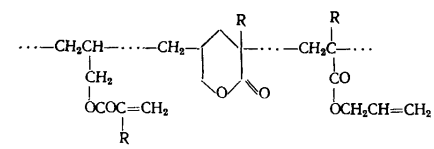
Arbuzova and coworkers[96–100] also studied the polymerisation of divinyl acetals; they obtained the cyclic polymers of the divinyl acetals of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and benzaldehyde. Sultanov and Arbuzova[101,102] established that, in contrast to divinyl acetals, allyl vinyl acetals and diallyl acetals give polymers in low yield, in which the fraction of cyclic units is small. It is interesting to note that ionic polymerisation of the divinyl acetals of formaldehyde[90,103] leads to the formation of only the cross-linked polymer, regardless of the reaction conditions.

The polymerisation of divinyl ketals [104], like that of divinyl acetals, leads to the formation of cyclic polymers containing, 1,3-dioxan rings:



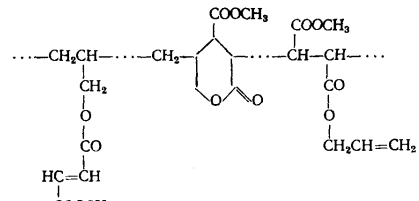
where R = R′ = CH_3; R = CH_3, R′ = C_2H_5; R,R′ = $(CH_2)_5$; R = R′ = C_6H_5.

The degree of cyclisation of asymmetric dienes, for example allyl esters of $\alpha\beta$-unsaturated acids, is as a rule low. Gindin et al.[105] indicated, in a discussion on the structure of the soluble polymers of allyl acrylate, the possibility that they have a cyclic structure. Several other workers[106–108] also obtained soluble polymers of allyl acrylate and allyl methacrylate, but the structre of the latter was not established. Schulz et al.[109] showed that, depending on the concentration of allyl acrylate in solution, the polymer contains at least 31% of six-membered lactone rings. In the radical polymerisation of allyl acrylate and allyl methacrylate[33] in dilute benzene solutions (5–10%) the yield of soluble polymers reaches 85%. By virtue of their considerable content of cyclic units, these polymers are relatively heat-resistant; the open-chain units contain both acryloyl and allyl bonds:



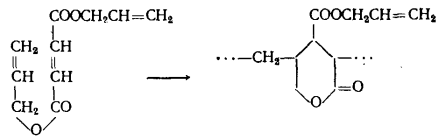
where R = H, CH_3.

The ionic polymerisation of allyl acrylate [110] under the influence of butyl-lithium proceeds exclusively at the acrylic double bond with formation of a non-cyclic polymer (m.p. 86–90°). Barnett et al.[111] studied the radical polymerisation of methyl allyl, methy-but-2-enyl, and methyl but-3-enyl esters of maleic and fumaric acids and found that the degree of cyclisation in the polymers obtained ($[\eta]$ = 0.036–0.072) amounted to 23–60%. The authors believe that the possible cyclic units are six- or seven-membered lactone rings (in the case of but-3-enyl esters) and therefore the structure of poly(methyl allyl fumarate), for example, is represented as follows:

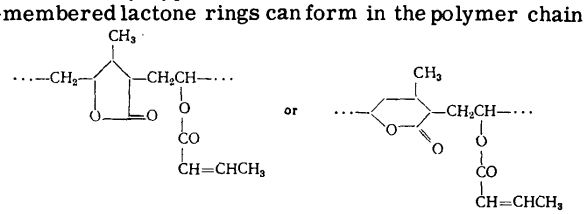


In the radical polymerisation of monoallyl esters of maleic and citraconic acids Arbuzova et al.[112] obtained cyclic polymers with a structure similar to that indicated

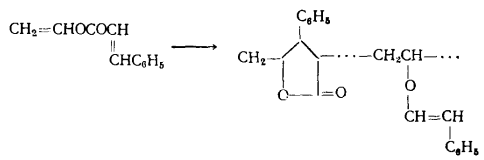
above. It was established that in the first stage of polymerisation of diallyl maleate [113] a soluble polymer is formed preferentially by a cyclic mechanism:



Rostovskii and Barinova [114] studied the radical polymerisation of vinyl crotonate in solution and obtained a soluble polymer ($[\eta] = 0.31$) containing about 50% of double bonds of the crotyl type. In their view both five-membered and six-membered lactone rings can form in the polymer chain:



In the polymerisation of vinyl *trans*-cinnamate in benzene solution in the presence of azoisobutyric acid dinitrile van Paesschen et al. [115] obtained a soluble polymer (yield 22–40%) which contained 80–85% of γ-lactone units and 15–20% of open-chain units:

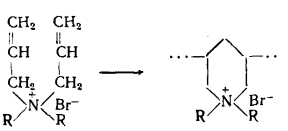


Roovers and Smets [116] studied the kinetics of the cyclic polymerisation of this monomer.

Barnett and Butler [117] investigated the polymerisation of allyl, β-methylallyl, γ-methylallyl, and propargyl vinylacetates and crotonates. The results showed that only allyl and β-methylallyl crotonates are converted into solid polymers (yield 10%, $[\eta] = 0.039–0.046$) with a degree of cyclisation of 25 and 31% respectively.

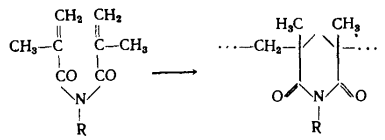
The cyclic polymerisation of non-conjugated oxygen-containing dienes was also investigated using the dimethacrylates of ethylene glycol and diethylene glycol as examples [118]. In contrast to the diallyl ester, the di-2-chloroallyl ester [33] readily forms a cyclic polymer which undergoes extensive dehydrochlorination as a result of the cyclisation of the monomer under the polymerisation conditions.

B. Polymerisation of nitrogen-containing dienes. The intermolecular-intramolecular polymerisation of non-conjugated dienes was in fact first used for the preparation of nitrogen-containing heterocyclic polymers. In their investigation of the radical polymerisation of unsaturated quaternary ammonium compounds Butler and coworkers [119–125] found that diallyldialkylammonium salts [12,13] form water-soluble polymers containing piperidine rings in the main chain:

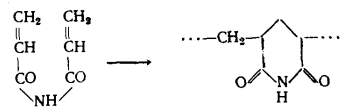


where R = H, CH_3, C_2H_5.

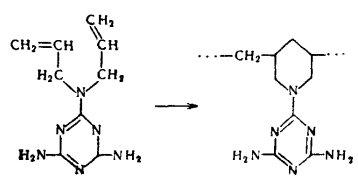
Sokolova and Rudkovskaya [126,127] synthesised six-membered nitrogen-containing polymers by the cyclic polymerisation of *N*-methyl- and *N*-ethyl-dimethacrylamides:



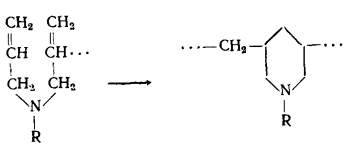
where R = CH_3, C_2H_5. In the polymerisation of *N*-acryloylacrylamide [128] a soluble polymer was obtained, whose chain units were identical with glutarimide:



Gibbs and van Densen [129] described cyclic polymerisation in the solid phase. On γ-irradiation (from a cobalt-60 source) of crystalline *NN*-diallylmelamine at room temperature, an acid-soluble polymer with a decomposition temperature of 250° and a molecular weight of 10 000–20 000 was obtained:



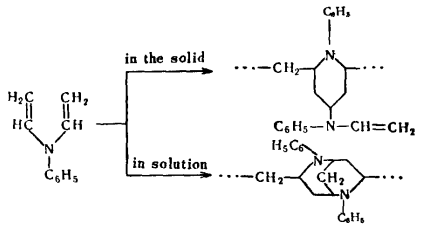
Matsoyan and coworkers [130] showed that introduction into diallylamine of polar substituents whose electron-acceptor group is lined directly with the nitrogen atom results in *N*-substituted diallylamine exhibiting a tendency towards radical polymerisation with formation of cyclic polymers containing piperidine rings:



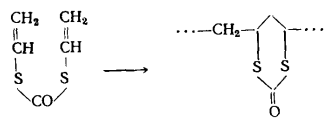
where R = CN, HCO, CH_3CO, C_2H_5CO, $ClCH_2CO$, CH_3OCO, C_2H_5OCO, C_6H_5CO, 4-$NO_2C_6H_4CO$, $C_6H_5SO_2$, 4-$CH_3C_6H_4SO_2$, $CSNHC_6H_5$. It was established that the capacity of *N*-substituted derivatives of di(methylallyl)amine [131] for cyclic polymerisation is much lower than that of the corresponding *N*-substituted diallyl derivatives. Similar cyclic polymerisation of *N*-diallyl compounds has been described by Ostroverkhov et al. [132]. In the polymerisation of allyl and ethyleneglycol esters of *N*-vinylcarbamic acid [109], *N*-allylacrylamide, and *N*-allylmethacrylamide [133] nitrogen-containing cyclic-linear polymers are also formed.

Chang and Price [133] described the synthesis of *NN*-divinylaniline and studied its polymerisation with the aid of an free-radical initiator. It was found that the polymeric unit forms as a result of the cyclisation of two *NN*-divinylaniline molecules and, depending on the method

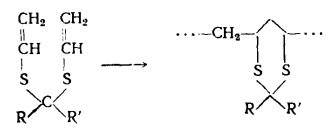
of polymerisation, the reaction leads to the formation of monocyclic or bicyclic units:



C. Polymerisation of dienes containing sulphur, silicon, phosphorus, and other elements. Ringsdorf and Overberger [134] studied the conditions of the polymerisation of *SS*-divinyl dithiocarbonate in the presence of a free-radical initiator and found that in dilute solutions a soluble cyclic polymer with a softening temperature of 300–310° is formed; a non-cyclic polymer obtained from the same monomer softens at 40–80°:



In the polymerisation of divinyl thioacetals and divinylmercaptans Matsoyan and Saakyan [135,136] obtained the sulphur analogues of polyvinylacetals in the form of elastic rubberlike substances. On hydrolysis these cyclic polymers converted into polyvinylmercaptan and on oxidation into the corresponding sulphones:

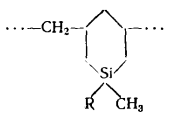


where R = R′ = H; R = H, R′ = CH_3; R = H, R′ = C_3H_7; R = R′ = CH_3. Ringsdorf and Overberger [137] also reported the cyclic polymerisation of the divinyl thioacetal of formaldehyde.

In contrast to diallyl sulphide and diallylsulphone, di-2-chloroallyl sulphide and di-2-chloroallylsulphone [33] are capable of polymerising in the presence of radical initiators with formation of cyclic sulphur-containing polymers which are extensively dehydrochlorinated under the reaction conditions.

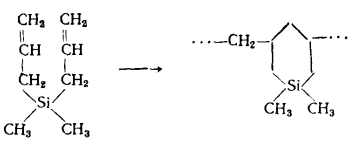
The possibility of the polymerisation of dialkenylsilanes in the presence of peroxide initiators was demonstrated by Korshak, Petrov, and coworkers [138–140]. The kinetics of the polymerisation of diallyldimethylsilane in the presence of t-butyl peroxide at 120–150° were investigated by Mikulasova and Hrivik [141]. Topchiev [142] demonstrated the possibility of the polymerisation of diallydimethylsilane and diallylmethylphenylsilane under the action of Ziegler type catalysts, but the structure of the products obtained, predominantly liquid, was not established.

Independently of Bogomol'nyi [144], Kolesnikov and coworkers [143] studied the polymerisation of diallyl derivatives of silicon. Under the action of the catalytic system $Al(C_2H_5)_3$–$TiCl_4$, diallyldiethylsilane gives a tetramer with six-membered cyclic units. Under similar conditions diallyldimethyl- and diallylmethylphenyl-silanes give rubber-like polymers, in the soluble fraction of which cyclic units with the following structure predominate:



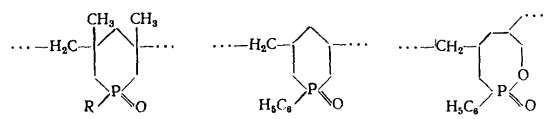
where R = CH_3, C_6H_5.

In a study of the polymer of diallyldimethylsilane obtained under the action of the $Al(iso\text{-}C_3H_7)_3$–$TiCl_4$ system, Marvel and Woolford [145] showed that the degree of cyclisation of the monomeric units in the polymer chain is 94%:



Butler and Stackman [146] studied the polymerisation of diallyldimethyl- and diallyldiphenyl-silanes with the aid of complex methal alkyl catalysts and obtained solid cyclic-linear polymers with m.p. 80–150° and $[\eta]$ = 0.065–0.13.

Berlin and Butler [147,148] studied the possibility of the cyclic polymerisation of phosphorus-containing non-conjugated dienes. They obtained soluble polymers (m.p. 85–185°, $[\eta]$ = 0.026–0.01) with a low content of residual double bonds on radical polymerisation in the solid state of methyl-, ethyl-, and dimethylallyl phenyl phosphine oxide, diallylphenyl phosphine oxide, and allyl phenyl allylphosphonate. The polymerisation proceeds by a cyclic mechanism with formation of phosphorus-containing heterocyclic polymers:

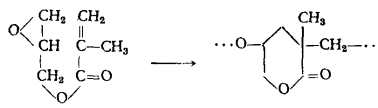


where R = CH_3, C_2H_5, C_6H_5. Unfortunately the structure of the soluble polymers of divinyl, diallyl and di(methylallyl) esters of various phosphorus acids has not been investigated, but is probably cyclic.

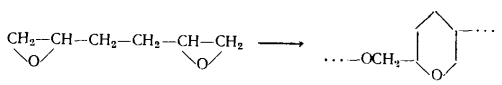
The synthesis of heterocyclic polymers from non-conjugated dienes containing other hetero-elements has been described in the literature — symmetrical diallyl compounds [143,149,150] in which the allyl groups are linked to the atoms of the following elements: Ge, Sn, Se, Ti, As, Pb, Zn, and others.

2. Polymerisation of Compounds of Other Types

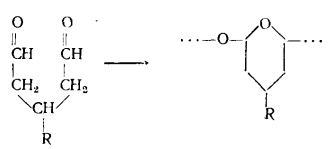
Arbuzova and coworkers [151,152] discovered the formation of a new type of cyclic polymers, from the glycidyl esters of acrylic and methacrylic acids. According to their data, both the epoxy-ring and the double bond of the monomer participate in ionic polymerisation [boron trifluoride etherate, aluminium trichloride], in contrast to radical polymerisation, with formation of cyclic units in the main polymer chain:



Stille and Culbertson [153] found that, under the action of the catalytic system PF_5–H_2O or $Zn(C_2H_5)_2$–H_2O, 1,2,5,6-diepoxyhexane polymerises with formation of a soluble polymer consisting of tetrahydropyran structural units:

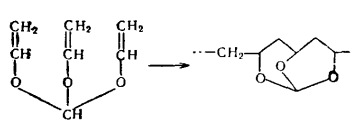


Under similar conditions 1,2,4,5-diepoxypentane yields insoluble polymers. A number of investigators have applied cyclic diene polymerisation to dialdehydes. In the polymerisation of glutaric aldehyde [154,155] in the solid state without initiator or in solution (in toluene) under the influence of various catalysts [$BR_3.(C_2H_5)_2O$, $Al(iso\text{-}C_3H_7)_3$, and others] soluble polymers with a small content of aldehyde groups are obtained. Infrared spectra of polyglutaraldehyde and also the polymers of β-methyl- and β-phenyl-glutaric aldehyde [156] show that the polymerisation involves intermolecular-intramolecular interaction of the two carbonyl groups of the monomers with formation of tetrahydropyran rings in the polymer chain:

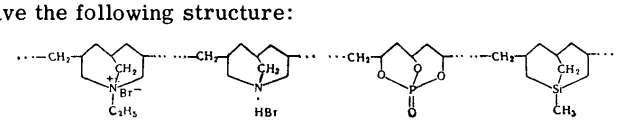


where R = H, CH_3, C_6H_5.

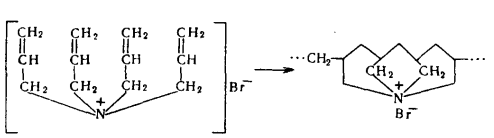
Matsoyan and coworkers [54] polymerised trivinyl orthoformate in solution in the presence of radical initiators and obtained a soluble bicyclic polymer (m.p. 250–260°) which is an ester derivative of poly(vinyl alcohol) and orthoformic acid:



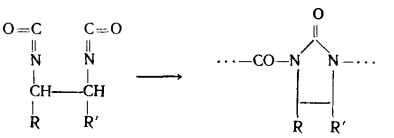
The possibility of the formation of nitrogen-, silicon-, and phosphorus-containing bicyclic polymers from branched trivinyl compounds has been demonstrated with triallylethylammonium bromide [157], triallylammonium bromide [54], trivinyl phosphate [54], and triallylmethylsilane [157] as examples. The chain units of the soluble polymers obtained have the following structure:



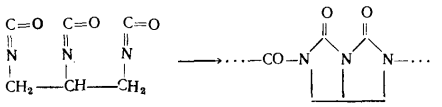
Trifan and Hoglen [157] have indicated that in the polymerisation of tetra-allylammonium bromide in dilute aqueous solution in the presence of t-butyl hydroperoxide (0.3%) a soluble polymer with tricyclic units in the main chain is formed:



King [158] polymerised aliphatic 1,2-diisocyanates in dimethylformamide solution in the presence of sodium cyanide and obtained cyclic-linear polymers between 290° and 365° and soluble in sulphuric acid, nitromethane, etc. According to his data, the cyclic polymerisation proceeds as a result of intermolecular-intramolecular interaction between the two nitrogen–carbon double bonds in the monomer:



where R = R′ = H; R = H, R′ = CH_3; R, R′ = $(CH_2)_4$. Under similar conditions glyceryl triisocyanate yields a bicyclic polymer melting at 365–400°:

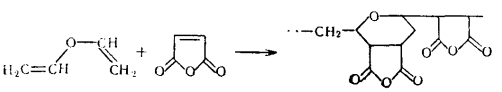


IV. SYNTHESIS OF CYCLIC COPOLYMERS

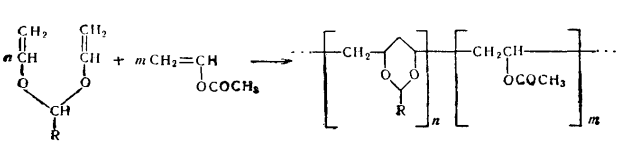
Even before the discovery of the cyclic polymerisation of non-conjugated dienes, the copolymerisation of vinyl monomers with isolated dienes was known; this reaction is widely used in the manufacture of cross-linked polymeric materials and cast articles.

Milford [29] studied the radical copolymerisation of 2,6-di(methoxycarbonyl)hepta-1,6-diene with acrylonitrile in solution and found that, when the concentration of the monomer mixture in the system is not higher than 10%, soluble linear copolymers with substituted cyclohexane rings in the chain are formed.

Butler [159] described the cyclic copolymerisation of vinyl ether, divinyl sulphone, and dimethyldivinylsilane with maleic anhydride, diethyl maleate, dimethyl fumarate, and vinyl acetate. Using vinyl ether and maleic anhydride as an example, Butler represents the formation of cyclic polymers in the following way:

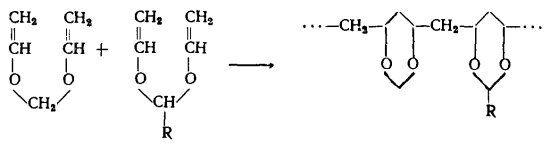


Matsoyan and coworkers [160–163] showed that the radical copolymerisation of the divinyl acetals of formaldehyde, acetaldehyde, butyraldehyde, isobutyraldehyde, and isovaleraldehyde with vinyl acetate proceeds by a cyclic mechanism; in the copolymer the divinyl acetal units form 1,3-dioxan rings. It was found that, whatever the molar proportions of the components and whatever the degree of the reaction, this type of copolymerisation leads to the formation of azeotropic copolymers, whose compositions are identical with those of the initial mixtures:

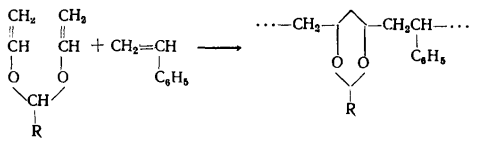


The possibility of cyclic copolymerisation of two diene monomers, forming rings on polymerisation, has been demonstrated [85] using the copolymerisation of the divinyl

acetal of formaldehyde with the divinyl acetals of acetaldehyde and butyraldehyde as examples[85]:

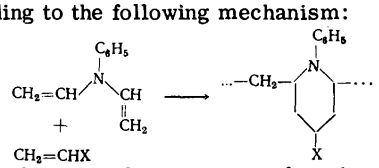


The copolymerisation of aliphatic divinyl acetals with styrene in the presence of benzoyl peroxide leads to the formation of the corresponding cyclic copolymers[164]. This reaction makes it possible to introduce simply and conveniently divinyl acetal units into the polystyrene chain:



Cyclic copolymers of similar structure were also obtained in the copolymerisation of the divinyl acetals of formaldehyde, acetaldehyde, and butyraldehyde with 2-methyl-5--vinylpyridine[165]. The possibility of cyclic copolymerisation of the divinyl acetal of butryaldehyde with monomers incapable of homopolymerisation — dimethylcrotonoyl carbinol and dimethylcrotonoylmethyl acetate — has been investigated[165]. It was found that in the presence of the cyclic divinyl butyraldehyde acetal these monomers are capable not only of copolymerisation but also of homopolymerisation.

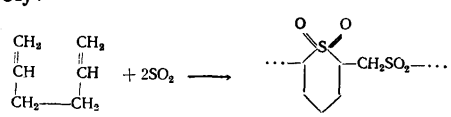
According to the data of Chang and Price[133], the copolymerisation of *NN*-divinylaniline, divinyl sulphone, and vinyl ether with styrene, *p*-methylstyrene, methyl methacrylate, etc. leads to the formation of six-membered cyclic groupings, each comprising one molecule of the diene and the vinyl component. Thus the cyclic copolymerisation of *NN*-divinylaniline with a vinyl monomer proceeds according to the following mechanism:



In a study of the copolymerisation of methacrylic anhydride with methyl methacrylate, styrene, acrylonitrile, etc. Hwa and Miller[166] found that soluble cyclic-linear copolymers are formed only when the reaction mixture is very dilute and when the degree of reaction is low. They showed that the usual equations for a binary system of vinyl monomers are applicable in the calculation of the composition of the cyclic copolymer when the degree of cyclisation of the non-conjugated diene component is relatively complete.

Michelotti[167] reported the possibility of cyclic copolymerisation of diallyl-2,3-epoxypropylamine with styrene.

Stille and Thomson[168] showed that the copolymerisation of hexa-1,5-diene with sulphur dioxide leads to the formation of a cyclic copolymer containing pentamethylene sulphone rings; the ratio of the initial components in the soluble part of the copolymer (m.p. 320–350°) is 1 : 2 respectively:



Roovers and Smets[116] established that the copolymerisation of vinyl *trans*-cinnamate with vinyl acetate, vinylpyrrolidone, methyl methacrylate, and styrene results in chain growth of the vinyl type due to the ester group of the diene as well as the cyclisation of the diene monomer into γ-lactone rings.

Avetyan et al.[169] showed that, in addition to the usual vinyl copolymerisation, cyclisation with formation of cyclopentanone rings in the main copolymer chain proceeds in the radical copolymerisation of isopropenyl propenyl ketone and isobutenyl vinyl ketone with acrylonitrile, vinylidene chloride, and 2-methyl-5-vinylpyridine. In the presence of radical initiators dibenzylideneacetone and maleic anhydride form an unsaturated cyclic-linear copolymer[44]. Matsoyan and Morlyan[170] studied the copolymerisation of ethynyldimethylvinyl carbinol with styrene, acrylonitrile, vinylidene chloride, methyl methacrylate, and vinyl acetate in the presence of benzoyl peroxide. They showed that the fraction of the copolymer consisting of the ethynyldimethylvinyl carbinol units contains cyclic units, like the homopolymers of ethynylvinyl carbinol[62,63].

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The foregoing review shows that cyclic polymerisation constitutes a new and rapidly developing field in polymer chemistry. Cyclic polymerisation makes it possible to prepare fundamentally new types of polymeric compounds with a wide variety of cyclic groupings in the chain, which were previously unobtainable; for this reason, synthesis of polymers and copolymers by cyclic chain polymerisation has been attracting recently the attention of a wide circle of investigators. There is no doubt that in future still further varieties of cyclic polymerisation will be discovered and that this method of synthesising polymeric compounds is one of the important means of obtaining polymers with valuable technical properties.

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THE SYNTHESIS OF MACROMOLECULAR COMPOUNDS BY RADIATION POLYMERISATION

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INTRODUCTION

At the present time, polymerisation is initiated chiefly by chemical methods in which the monomers or their solutions are treated with initiators for polymerisation taking place by a radical mechanism, or catalysts for ionic polymerisation. The use of thermal and photochemical method of initiation is limited — for the first because of the unfavourable conditions for the development of chains at elevated temperatures and the secondary processes which take place, and for the second because of the low efficiency and the complexity of the technological layout, associated chiefly with the influence of the optical properties of the medium on the course of photochemical reactions.

Recently, the attention of many research workers has been drawn to a new method of polymerisation — radiation polymerisation — in which the chain process is initiated by the action of ionising radiation. The first observations of the formation of polymeric (resinous) substances under the influence of the radiation from radium and radon were made at a very early date, but the development of radiation polymerisation as an independent branch of the chemistry of macromolecular compounds is a recent phenomenon. It appears that in a few years this new method will be recognised as an effective industrial method for the synthesis of certain polymeric products.

Problems of radiation polymerisation have been examined in a number of general papers and reviews[1-17], which give data characterising chiefly the fundamental features of the method, in particular the mechanism of radiation-chemical initiation, the influence of various factors (including such specific factors as the dose and dose rate) on the reaction rate, sensitisation in multicomponent systems, polymerisation in inclusion compounds, etc. Special reviews devoted to radiation polymerisation in the solid phase[18-23] and a review of the patent literature[24] have been published. No systematic review of data on the use of radiation-chemical initiation for the polymerisation of various monomers according to classes has

been published, however. The aim of the present work is to fill this gap.

Radiation polymerisation has a number of advantages over other methods for the preparation of polymers.

1. It makes it possible to obtain polymeric products based on monomers whose polymerisation under ordinary conditions either does not take place at all or can be achieved only with considerable difficulty. Such monomers include, in particular, certain fluorine-containing monomers which give valuable heat-resistant and chemically stable polymers of practical importance[14], monomers with a symmetrically-substituted double bond[25-27], and allyl monomers[28].

2. Radiation polymerisation is the simplest and most effective method for polymerising monomers in the solid phase[14], and also in channel[29] and layer[30] inclusion compounds.

3. The radiation method makes it possible to obtain highly pure polymers containing no residual initiators, catalysts, or other auxiliary polymerisation agents, whereas this is unavoidable in polymerisation by the usual methods[2]. These impurities are often responsible for a significant deterioration in the operational properties of the polymers; this is of particular importance for polymers used in radio-electronics and medicine, where these impurities have a harmful influence[31].

4. With radiation initiation, polymerisation can be carried out at reduced temperatures, at which the conditions of chain growth are favourable for the formation of macromolecules with only minimal degrees of branching; this leads to an improvement in the properties of the polymeric materials[2].

5. Radiation polymerisation takes place more smoothly than ordinary polymerisation and enables the reaction rate to be regulated[2]. In "material" initiation the rate decreases as the initiator (or catalyst) is used up, and with an exothermic process increase in temperature leads to an increased rate of dissociation of the initiator, resulting in a change in the rate of the process[9]. With radiation initiation, however, analogous increase in temperature has almost no influence on the concentration of radicals or ions initiating the polymerisation, since this concentration is determined chiefly by the intensity of the irradiation (dose rate). By varying the latter, it is possible to polymerise monomers with appreciable quantities of inhibiting additives, whose action is suppressed[2].

6. The radiation method sometimes makes it possible to produce polymer manufactured parts "in situ" in construction where access is difficult ("imprinting" linings, one-piece parts, etc.)[31].

7. Radiation polymerisation in certain instances makes it possible to obtain finished textile fibres in a single operation by irradiating the crystalline monomer[32].

The use of radiation-chemical initiation naturally involves a number of difficulties, of which the following may be noted: special requirements have to be satisfied in the design of the apparatus, associated with the use of penetrating radiation (safety precautions), and also with the need, in most instances, to create in the reaction zone a field with uniform radiation density; the possibility of secondary processes and side-reactions: cross-linking or degradation of the resulting polymers and radiolysis of the monomers.

These difficulties are not insuperable, however. It appears to be possible to find solutions to the engineering and technological problems and to choose reaction conditions which will satisfy the requirements made of the apparatus and will make it possible to carry out the process with maximal rate of polymerisation and relatively low yields of side products. Sometimes it is possible in principle to make the process continuous, with removal of the resulting polymer from the irradiation zone. In individual instances it is possible to make use of the cross-linking of the resulting polymer and to combine the preparation of the polymer and its vulcanisation in a single process. It should also be noted that the radiolysis products contaminating the finished polymer do not lead to a deterioration in its electrophysical properties, although they may sometimes have a plasticising action.

We shall examine the results of published work on the use of ionising radiation for the synthesis of polymeric products from monomers of different type. The problems of radiation copolymerisation, including graft copolymerisation and telomerisation, are not examined here, since they are of independent interest. The monomers are grouped according to the usual classification of organic compounds with allowance for the nature of the structural elements by which polymerisation is brought about.

1. RADIATION POLYMERISATION OF ALKENES

Ethylene, depending on the polymerisation conditions, forms products with different molecular weights, from liquid oils and waxy substances to hard plastics with a fairly high degree of crystallinity[1]. Macromolecular products are obtained only under pressure (~ 300–400 atm), but this pressure is much lower than the pressures used in the production of ordinary "high pressure" polyethylene (1500–3000 atm at 150–250°). The properties (density, degree of crystallinity, degree of branching) of "radiation" polyethylene are similar to those of polyethylene obtained at low pressures. It has excellent dielectric properties including, in particular, low dielectric loss at high frequencies[1]. To give ordinary "low pressure" polyethylene these properties, special purification of the polymer from traces of catalysts is necessary. The cost of low-pressure polyethylene purified in this way is 1.5–2 times greater than the cost of radiation polyethylene. The radiation process is free from the danger of explosion, is readily controlled, and takes place at low temperatures[33] with values of G up to 1 130 000 (at 200° and 850 atm)[34]. Economic calculations show that when fuel elements are used, the radiation method for preparing polyethylene can compete with ordinary methods[35]. The requirements to be satisfied by the chief technological characteristics of apparatus for the radiation polymerisation of ethylene on the industrial scale have been formulated[36]. The polymerisation of ethylene under the influence of γ-radiation is carried out from the gaseous phase[37-41] and in liquid medium[24,42]. Study of the heterogeneous polymerisation of ethylene[43,44] under a pressure of 300–400 atm at temperatures below the melting point of polyethylene (25°) showed that the process takes place in the kinetic range[45]. The radiation polymerisation of ethylene in solutions has been studied[41,46], but here products with molecular weight not exceeding 40 000 are formed. In aqueous solutions in

the presence of Ag salts the radiation yield G reaches 60 000 molecules per 100 eV.[47] Irradiation of ethylene in the solid state (-196°) in a Van de Graaf electrostatic generator (3 MeV) gives a negligibly low yield of polymer (G = 2.5). The results of experiments on the irradiation of a mixture of ethylene and deuteroethylene lead to theories of an ion-molecular mechanism[48].

The molecular weight of radiation polyethylene may reach 800 000[41] and even 1.5 million.[53] The polymer has a higher density (0.945–0.975 g cm^{-3}) and crystallinity than high-pressure polyethylene but its tensile strength is about the same. The macromolecular chain of radiation polyethylene has a low degree of branching[49].

Of particular interest is the polymerisation of ethylene on Ziegler catalysts — halides of Ti, V, Cr, Co, Fe, Zr, etc. — in which the part of cocatalyst is played by the ionising radiation. A solution of the metal halide (for example, a solution of $TiCl_4$ in heptane) is irradiated at low temperature, after which gaseous ethylene is passed through the irradiated solution; under these conditions the ethylene polymerises. Studies of this type are directed towards an investigation of the role of the components and the mechanism of action of the Ziegler–Natta catalysts[50–52]. The action of γ-radiation on a mixture of ethylene and carbon dioxide at temperatures from -78° to +204° gives liquid and paste-like polymers of carboxylic acids with a linear carbochain structure and molecular weight up to 660 ($G_{-C_2H_4} \simeq$ 310 molecules per 100 eV).[53] The radiation-catalytic method has been used to prepare higher carboxylic acids with m.p. 121–123° and M = 3000.[54]

The polymerisation of propene at pressures up to 160 atm, temperatures from -75° to +200° and a dose rate of 400 r s^{-1} gives oily products with low molecular weights in the range 112–200 (G varies in the range 800–4400 molecules per 100 eV).[55] Work has also been carried out on the radiation polymerisation of propene at high pressures of 5000–17 000 atm and 21–83°.[56,57] The maximal degree of polymerisation reached 75 and the values of G reached 108 000. The results obtained indicate that this process takes place by a radical mechanism[56]. Radiation polypropene is soluble in benzene at room temperature.

2-Methylpropene is a convenient material for studying the cationic mechanism of radiation polymerisation[58–69]. 2-Methylpropene does not polymerise at 0° and higher temperatures. Polymerisation from the gaseous phase gives only low-molecular-weight products[70]. At low temperatures (-78°) in the presence of electron-accepting solid additives or solvents, 2-methylpropene gives a polymer with high molecular weight and the same properties as that obtained by ordinary polymerisation. The influence of the purity of the monomer on the yield and molecular weight of radiation polyisobutene [poly-(2-methylpropene) (Ed. of Translation)] has been established[55]. Oxygen and more particularly water have an inhibiting influence. G may be increased to 2 million by polymerisation under sterile conditions in the presence of specially treated zinc oxide[12]. A polymer with M = 3.759 million was obtained at -110° and a dose of 24 Mrad.[67]

The radiation polymerisation of higher alkenes — pentenes[71], hex-1-ene[72], n-heptene (in the presence of $TiCl_4$)[73], oct-1-ene[72–74], oct-2-ene, 2,2,4-trimethylpent-2-ene[74], 2,4,4-trimethylpent-1-ene[75,76], and hexadec-1-ene[77] — leads to the formation, for the most part, of liquid and viscous polymers of low molecular weight.

2. ALKADIENES

Diene hydrocarbons are polymerised with low radiation-chemical yields. The radiation polymerisation of butadiene "in bulk"[78–80] at temperatures from 0° to -196° gives a polymer containing the same relative quantities of *cis*-1,4-, *trans*-1,4-, and 1,2-linkages as the product obtained by the cationic mechanism. This indicated that at low temperatures the radiation polymerisation of butadiene also takes place by a cationic mechanism[79]. In all instances, including those where halogen-containing solvents were used[81] (apart from one[78], where the degree of conversion was very small), low-molecular-weight viscous polymers are formed. Channel polymerisation in urea complexes leads to the 1,4-*trans*-structure with m.p. 135°.[82]

A method has been described in a patent[83] for preparing macromolecular polybutadiene ($[\eta]$ = 1.8) at +40° and a dose of 0.5 Mr in an emulsion; the product has the microstructure: 1,4-*trans* 57%, 1,4-*cis* 20%, and 1,2 23%. A polymer with M = 100 000 was obtained by irradiation in nitromethane at -100°.[84]

The radiation polymerisation of isoprene "in bulk" gives viscous polymers[85–88]. As for butadiene, the possibility of polymerisation at low temperatures by an ionic mechanism has been demonstrated[85,87]. The microstructure (at 20°) includes up to 8% 1,2- and 3,4-linkages and up to 84% 1,4-linkages, including 15% 1,4-*cis*-linkages. The concentration of 1,4-*cis*-linkages increases to 36.4% with increase in temperature to 40°. Irradiation in the presence of $TiCl_4$ increases the rate of the process, which takes place by a cationic mechanism[89]. The sensitisation of the polymerisation of isoprene by carbon tetrachloride has been studied[86,90]. The radiation polymerisation of isoprene in clathrate complexes with 4,4'-dihydroxytriphenylmethane gives a polymer with a ratio of *cis*-1,4- to *trans*-1,4-linkages equal to 1 : 9, with almost complete absence of the 1,2- and 3,4-structures[91]. A polymer with M = 200 000 was obtained by irradiating isoprene in a Van de Graaf generator at -100°.[84]

Piperylene "in bulk" under the influence of radiation also forms a viscous polymer with $G \simeq$ 20–30 molecules per 100 eV. The sensitisation of its radiation polymerisation by noble gases (argon and krypton) and also by carbon tetrachloride has been noted. The decreased concentration of double bonds in the polymer is due to possible cyclisation[92].

The microstructure of the polymer, studied by infrared spectroscopy[92,93] and ozonisation[93], consists chiefly of the 1,4- and 1,2-*trans*-linkages (64–67%). The concentration of 1,2-linkages is 17.4% and that of 3,4-linkages (vinyl group) is 3–6.5%. "Channel" polypiperylene, prepared in the complex with urea[94], is more regular and contains no 3,4- or *cis*-linkages.

2,3-Dimethylbuta-1,3-diene and cyclohexa-1,3-diene give high-melting crystalline polymers with the *trans*-structure when their complexes with thiourea are irradiated[29,95,96]. Ammonia has a marked inhibiting action on the polymerisation of cyclopenta-1,3-diene at -78°;[97,98] this may be due to the transfer of a proton from the hydrocarbon ion to NH_3 and also to aminolysis of carbonium ions[99]; methylene dichloride has a marked sensitising influence on the polymerisation[100].

In the irradiation of dienes, polymerisation is accompanied to some extent by radiolysis[101]. It has been suggested that

the radiolysis products may inhibit the polymerisation.

3. HALOGENO-DERIVATIVES OF ALKENES AND ALKADIENES

Of the halogeno-derivatives of the alkenes, the fluoroalkenes have been most extensively studied. Tetrafluoroethylene is one of the monomers most readily polymerised under the influence of radiation. The radiation polymerisation yield is exceptionally high and reaches 800 000 molecules per 100 eV; the organisation of an industrial process for the radiation polymerisation of Fluoroplast can thus be regarded as one of the first tasks in radiation technology. The radiation polymerisation of tetrafluoroethylene takes place from the gaseous phase [102,103], "in bulk", in chloroform [102,104], in aqueous medium [104], at low temperature in the liquid phase [105], and in the solid phase [106-108]. A post-effect is observed [102,104]. The radiation polymerisation of trifluorochloroethylene "in bulk" has been studied over a wide range of dose rate and temperature [104,109,110]. The polymerisation was first studied by Lazar [111]. The polymer forms a solid phase insoluble in the monomer. G reaches values of 10 000 molecules per 100 eV. In halogen-containing solvents ($CHCl_3$, CCl_4, $CFCl_2-CF_2Cl$), polymers with melting point of the crystalline phase in the range 80–200°, have been obtained [112] depending on the dose rate. The polymerisation takes place by a radical mechanism and gives a product of the Fluoroplast-3 type. A post-effect is observed. Vinylidene difluoride also polymerises under the influence of γ-radiation [113-115]. The rate of polymerisation decreases in the order: tetrafluoroethylene–vinylidene difluoride–trifluorochloroethylene [114]: the corresponding values of G (molecules of monomer per 100 eV) are 10^6, 10^5, and 10^4. The marked induction effect is due to contaminants, particularly oxygen [114]. The activation energy (6–8 kcal mole^{-1}) and dose rate exponent (0.6) indicate a radical mechanism. Complete conversion of the monomer requires a dose of 24 Mr. Radiation polymerisation of vinyl fluoride at a dose rate of 34 r s^{-1} leads to the formation of waxy products. A radical mechanism is indicated [116]. $G \simeq 10^3$ molecules per 100 eV. [115] C_3-Fluoroalkenes with different degrees of fluorination and the monomer $CH_2=C<^{CF_3}_{CF_3}$, under the influence of radiation, form polymers with M = 510–800 in the form of viscous liquids and wax-like products with G = 9–350 molecules per 100 eV. [117] Perfluoropropene, [118,119] perfluoro-2-methylpropene, [119] and perfluoropentylpropene [119] form oligomers at extremely high doses (~200–600 Mr). These liquid "radiation" fluoropolymers can be used as heat-resistant lubricants. Irradiation of n-perfluorohept-1-ene under a pressure of 10 000–15 000 atm gives a solid polymer with M = 5000. [120] The highest degree of polymerisation, equal to 76 ± 8, was observed at a pressure of 17 000 atm, 189°, and dose rate 0.0027 Mrad h^{-1}. [56] It should be emphasised that for most of the fluorinated monomers examined, radiation polymerisation provides the only possible method of conversion into polymers.

Vinyl chloride in the gaseous phase has been polymerised by α-particle bombardment [121,122] with the formation of liquid and solid polymers and radiolysis products — hydrogen and methane. The polymer formed under the influence of γ-radiation consists of a white powder which swells readily in the reaction medium, and on further irradiation forms a red solid monolithic material. Oxygen inhibits the polymerisation [123,124] but mercury at 10–95° sensitises it [123]. At a pressure of 1.5 atm and room temperature, $G \simeq 900$ molecules per 100 eV. In the liquid phase ("in bulk") at room temperature a polymer analogous to that obtained by ordinary polymerisation is formed [78,125-128]. The kinetics of polymerisation are typical of those for a hetero-phase process [127,129]. A post-effect is observed. "In bulk" at -20° with a dose of 0.2–0.5 Mrad, a product with glass point 100° is formed (with "material" initiation, the glass point of the polymer is 75–80°) [127]. Radiation poly(vinyl chloride) has not only an increased heat resistance, but also a high purity, which distinguishes it from the polymers obtained by the usual methods [125,130]. It may find application in fields where prolonged stability to high temperatures is required [1]. There are patents on the continuous production of poly(vinyl chloride) with initiation by γ-radiation [125,131]. Vinyl chloride polymerises in the vitreous state in a solid dispersion (mineral oil, etc.) [132]. Polymerisation of the monomer itself in the solid phase is not observed, however [133,134].

Channel polymerisation of vinylidene dichloride (complex with thiourea) [95] gives a brown polymer identical with that obtained in the usual way. No polymerisation of vinylidene dichloride is observed in the solid phase at -196° under the influence of γ-radiation [18]. The formation of polymeric products by the γ-irradiation of *cis*- and *trans*-1,2-dichloroethylenes has been studied [26,135]. Only the *trans*-isomer forms solid polymers. The total radiation yield for *trans*-1,2-dichloroethylene amounts to 204–239 molecules per 100 eV; the concentration of solid polymer in the polymeric products reaches 24.8%. For *cis*-1,2-dichloroethylene, G = 134–138. Trichloroethylene and tetrachloroethylene have values of G (molecules per 100 eV) equal to 31–34 and 9 respectively [26]. Liquid and waxy oligomers are formed from trichloroethylene. Thus increase in the number of chlorine atoms in the ethylene molecule leads to an increase in the stability of the monomer towards radiation.

Vinyl iodide in the pure state or in concentrated solutions does not polymerise under the influence of X-rays. In solutions in CCl_4 (concentration less than 80%), $CHCl_3$ (concentration less than 60%), and CH_2Cl_2 (concentration less than 45%), however, it forms solid white polymers which are stable in air in diffused light for a period of two months; the temperature of decomposition in a vacuum is 97°. [136]

Perfluorobutadiene at a dose of 225.6 Mr forms an oligomer in 55% yield [40,119] and 4-chlorodecafluorohepta-1,6-diene forms a polymer with 100% conversion at 150°, a pressure of 1 atm, and a dose rate of 0.2 Mrad h^{-1} with irradiation for 71 h. The low characteristic viscosity of the polymer (0.09) can be increased to 0.60 by carrying out the polymerisation at a dose rate of 0.003 Mrad h^{-1} for 113 h at 147° and a pressure of 13 600 atm; [56] here a solid product is formed.

When irradiated "in bulk", Chloroprene [2-chlorobuta-1,3-diene (Ed. of Translation)] forms a cross-linked product (μ-polymer). Formation of soluble α-poly(chloroprene) is achieved by the addition of stabilisers which regulate the molecular weight and the process of structure formation [137,138]. The properties of the radiation elastomer are similar to those of GN Neoprene [137]. 2,3-Dichlorobuta-1,3-diene in its complex with urea and thiourea is polymerised completely in an electron

beam (800 keV, dose rate 2.3×10^5 r s^{-1}) in several seconds with the formation of a highly crystalline *trans*--1,4-polymer with regular structure[82,95].

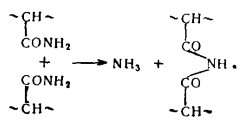
4. UNSATURATED CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Acrylic, methacrylic, and butadiene-1--carboxylic acids polymerise under the influence of γ-radiation in the solid phase[133,134,139]. In the case of acrylic and methacrylic acids at -18° the polymerisation is very rapid (rate of conversion 400% h^{-1})[133]. Butadiene-1--carboxylic acid polymerises spontaneously and forms a cross-linked product[139]. Its closest homologue — sorbic acid — undergoes 1,4-polymerisation in the solid phase and in solvents by a radical mechanism yielding amorphous soluble polymers with $[\eta]$ up to 1.0.[140] Potassium, sodium, and lithium acrylates and methacrylates, rubidium and calcium acrylates, and barium methacrylate also polymerise in the solid phase[18,141,142]. The difference in the crystalline structure of the monomers determines their relative rates of polymerisation. Marked differences are observed between the ease of polymerisation of the hydrated salts and the anhydrous forms. For example, at a dose of 0.8 Mrad under identical conditions, the conversion of barium methacrylate dihydrate amounts to 55%, while that of the anhydrous monomer is 1%.[142] The sodium, potassium, and barium butadiene-1-carboxylates are fairly stable to γ-radiation[139].

The polymerisation of methyl acrylate "in bulk", initiated by γ-radiation, is very rapid at room temperature and is accompanied by a marked gel-effect[78,143]. Polymerisation in an atmosphere of air (dose 40 Mr) gives a colourless transparent elastomer. Its density is 25% greater than that of the ordinary polymer. The increase in weight of a specimen immersed in water for 24 h is 0.4%.[40] Very slight sensitisation is observed in CCl_4 solution[144]. Polymerisation takes place by a radical mechanism at -78° in polar solvents[145]. Almost no polymerisation takes place in the solid phase (at -78° and -196°)[18]. Ethyl acrylate polymerises readily at low temperatures[12] and in an emulsion at 25°.[146] Methyl methacrylate (MMA) has been studied fairly systematically. For polymerisation "in bulk" the degree of conversion and molecular weight of the polymer are increased at higher temperatures. The gel-effect is very marked and is appreciable even at a degree of conversion equal to 2%.[78] The polymerisation of MMA has been studied in the presence of solid additives[147-149] and in various solvents: methyl acetate[150-152], ethyl acetate[150], carbon tetrachloride[150-153], benzene[78,150-152], its mixture with acetone[154], methanol[78], isopropylamine[155], and dimethylformamide[156]. The rate is decreased in benzene, whereas sensitisation is observed in CCl_4, $CHCl_3$, and dioxan[157]. Special technological apparatus has been developed and tested under different conditions[158], indicating an attempt to introduce a radiation method for the polymerisation of MMA. The monomer itself does not polymerise in the solid phase[18,156] but polymerisation can be achieved by adding alkanes[132,156]. A kinetic study has been made of the radiation polymerisation of cetyl methacrylate in the liquid and solid phases[159-161]. The rate of polymerisation of the crystalline monomer is fairly high initially and decreases with increase in the degree of conversion, indicating degeneration of the autocatalytic nature of the polymerisation in the solid phase[162]. The degree of polymerisation at 60° reaches about 30 000.

Diacrylates and dimethacrylates (octamethylene diacrylate, ethylene dimethacryalte, and octamethylene dimethacrylate) are polymerised under the influence of fast electrons (800 keV)[163]. The polymerisation of octamethylene dimethacrylate has been studied in more detail than that of the others. Its rate at room temperature is 45 times that of the polymerisation of MMA. A crosss-linked polymer in the form of a gel is produced in several seconds. Since the diffusion of the growing chains in such a short time interval is almost negligible, the shape of the resulting polymer reproduces exactly the geometry of the electron beam falling on the monomer[1]. 2,2,3,3,4,4,4-Heptafluorobutyl acrylate at a dose of 220 Mfer is converted completely into a cross-linked rubber-like polymer which softens and undergoes degradation at 150°.[119] Here the polymerisation takes place at both the C=C and the C=O bonds.

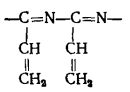
The radiation polymerisation of acrylamide in aqueous solutions has been studied[164,165]. Irradiation of solutions with a monomer concentration greater than 10% gives cross-linked products with liberation of ammonia, apparently as a result of reaction between the chains with the formation of an imide bridge



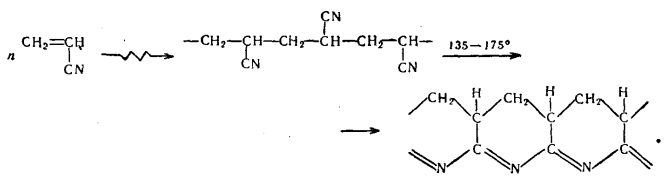
Acrylamide polymerises readily in the solid phase[133,134,166-175]; under pressure the rate increases close to the melting point of the monomer[176,177]. It is suggested that the solid-phase polymerisation takes place by a radical mechanism[178,179]. Methacrylamide also polymerises in the solid phase[168,175,180]. The yield of polymer is much greater for irradiation in air at 32° than for irradiation in nitrogen[181]. Post-polymerisation is observed[180]. *N*-Arylmethacrylamides (the *o*-chloro-, *o*-butyl-, and *o*-ethoxy-derivatives) also polymerise in the solid phase at 20° ± 3°.[180] The solid-phase polymerisation of the *N*-phenyl- and *p*-biphenylylene-derivatives was observed directly in an electron microscope under the initiating influence of the electron beam[182].

Detailed studies have been made of the radiation polymerisation of acrylonitrile "in bulk"[183-186] and in various solvents: dimethylformamide[156,187-191], triethylamine[187,192], isopropylamine, acetone, toluene[87], ethyl chloride, acetonitrile[58,192], butyronitrile[192], methanol[1], and water[193-195]. In polymerisation "in bulk" the polymer separates in the form of aggregates of particles[78]. A clearly defined post-effect is observed. In polymerisation in aqueous solutions under the influence of γ-radiation, a number of sulphates exhibit an inhibiting influence[195]. The addition of substances with electron-acceptor character (ethyl chloride, ethyl acetate, acetonitrile, and butyronitrile) to a solution of acrylonitrile in triethylamine at -78° inhibits polymerisation but the addition of substances with electron-donor character (pyridine)[192] or the addition of semiconducting oxides of the *p*-type[147,148], accelerate the polymerisation. It has been shown that the radiation polymerisation of acrylonitrile may take place both by a radical mechanism and by an ionic mechanism; these mechanisms predominate in the ranges of elevated and reduced temperatures respectively[196]. A patent[197] has proposed that the efficiency of radiation polymerisation be

increased by using a platinum electrode in contact with the polymerisation system to remove the electrons which accumulate during irradiation. In this way the yield of polyacrylonitrile is increased from 6.5% to 19.6% for a dose of 7.3 Mr and a dose rate of 0.09 Mr h^{-1}. In the opinion of Japanese authors[198], the polymerisation of acrylonitrile in liquid ethylene gives a product which contains, in addition to polyacrylonitrile with ordinary structure, chains with the following structure:



A post-effect is observed in the solid-phase polymerisation of acrylonitrile[156,175,196,198-207]. The molecular weight of the polymer reaches 200 000 or more. Polyacrylonitrile obtained at temperatures from -94° to -196° is a syndiotactic polymer; on thermal treatment the $-C\equiv N$ group is readily converted into the $-C=N-$ group[208]:



At a dose of ~200 Mr perfluoroacrylonitrile forms a polymer with low molecular weight in 20% yield[119]. The behaviour of methacrylonitrile is analogous to that of acrylonitrile[209]. In the solid phase at low temperature, the polymer is formed, in the opinion of the authors, by opening of the double carbon–carbon and triple carbon–nitrogen bonds[210]. It is suggested that the product is a syndiotactic polymer whose $-C\equiv N$ groups, unlike the analogous groups of the acrylonitrile polymer, are converted into $-C=N-$ groups without the use of elevated temperatures, apparently due to the influence of the methyl group[208].

5. VINYL ESTERS AND ETHERS

The radiation polymerisation of vinyl acetate is extremely sensitive to traces of contaminants. The polymerisation "in bulk" has been studied under conditions of initiation by γ-radiation[78,150] and in a reactor with filtered-neutron irradiation[211]. Studies have been made of the influence of 70 different additives, of which the most effective were found to be acids and their anhydrides[212]. It was established that the molecular weight of the polymer decreases with increase in temperature[213]. A patent[214] has proposed a method for carrying out the polymerisation in different solvents using various radiation sources with subsequent hydrolysis of the polymer to poly(vinyl alcohol). Study of the polymerisation in the solid phase with irradiation by 1.6 MeV electrons showed that the reaction rate is much less than that in the liquid phase; the rate of polymerisation of the solid monomer in the vitreous state is greater by one order of magnitude than that in the crystalline state[203,204]. It has been shown that the polymerisation takes place only in the beam; there is no post-effect. Vinyl stearate[133] and octadecyl vinyl ether[215] are polymerised under the influence of ^{60}Co γ-radiation above and below the melting point.

The polymerisation of pentafluorophenyl trifluorovinyl ether and phenyl trifluorovinyl ether was achieved only by using radiation initiation (γ-radiation) under a pressure of 12 000–14 000 atm at 100–103°.[56] The radiation polymerisation yield for a dose rate of 0.003 Mrad h^{-1} is 283 molecules per 100 eV for the first and 1190 molecules per 100 eV for the second.

6. VINYL DERIVATIVES OF CARBOCYCLIC COMPOUNDS

The radiation polymerisation of styrene "in bulk" has been studied under conditions of initiation by γ-radiation[216,217]. The polymer formed by complete conversion has a higher heat resistance than the ordinary polymer[2]. Polymerisation "in bulk" by radiation from an atomic reactor (neutron irradiation filtered with cadmium foil) shows a low degree of conversion (0.79% after 60 min)[211]. Macromolecular radiation polystyrene with an average molecular weight of 70 000 was obtained by Abkin and coworkers by the polymerisation of styrene in ethyl chloride solution at -78°.[61,218] The efficiency of the ionic polymerisation of styrene is increased in solvents with high dielectric constant (methylene dichloride)[219,220], in the presence of SiO_2 and other mineral additives at -78°.[221-223] Bromoform is an extremely effective sensitiser[224]; white phosphorus accelerates the polymerisation slightly[225]. The radiation polymerisation of styrene in the presence of the initiator benzoyl peroxide has also been studied[226]; the rate of polymerisation is ten times the value calculated assuming additivity, indicating effective transfer of excitation energy from the styrene to the benzoyl peroxide. Data have been obtained indicating an ionic mechanism for the polymerisation of styrene under ordinary conditions[227] and a radical mechanism in the solid phase (vitreous state in mineral oil)[132]. It has been shown that the polymerisation of styrene and 2,4-dimethylstyrene takes place simultaneously by ionic and radical mechanisms[228,229].

α-Methylstyrene at room temperature forms low-molecular-weight polymers with an exceptionally low rate of polymerisation[230]; the author considers that the polymerisation takes place by a radical mechanism. At -78° the reaction takes place by an ionic mechanism[59]. The anhydrous monomer gives a polymer with degree of polymerisation 15–45 and G = 8000 molecules per 100 eV.[231] Macromolecular poly-(α-methylstyrene) (average molecular weight 50 000) is formed by the action of γ-radiation at 25° and a pressure of 10 000 atm (G = 18 molecules per 100 eV)[129]. In solution, m- and p-methylstyrenes polymerise by a radical mechanism at 25° and by a cationic mechanism at -65°.[232]

p-Acetamidostyrene polymerises instantly under the influence of γ-radiation in the solid phase; this may be of practical importance for the production of textile fibres in a single operation by irradiation of the crystalline monomer[32].

β-Pinene also polymerises under the influence of radiation[231,233,234]. Traces of water decrease the rate of the process considerably. When the β-pinene is dried the values of G increase to 370–1055 molecules per 100 eV.[231] Attention has been drawn to the need to purify the monomer not only from traces of moisture but also from oxygen. Irradiation of the liquid monomer with a dose of ~4 Mrad gives a solid polymer in 45% yield; this is precipitated during the polymerisation and is stable at 230° in a vacuum. The polymerisation apparently involves opening of the double bond and it is suggested that elements of a camphene structure may be formed by rearrangement. Data

obtained by infrared spectroscopy and NMR also indicate the presence of unsaturated groups in the microstructure[233].

7. VINYL DERIVATIVES OF HETEROCYCLIC COMPOUNDS

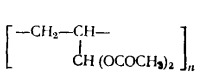
The radiation polymerisation of vinylpyrrolidone has been carried out in aqueous, alcoholic, and chloroform solutions[1]. Poly(vinylpyrrolidone) is important in medicine (blood plasma substitute). It can also be used in the dyestuffs industry, for cosmetics, and for other purposes. Advantages of its production by radiation polymerisation include the slightly narrower molecular-weight distribution and the possibility of organising a continuous process[1,9]. Vinylpyrrolidone also polymerises in the solid phase[18,235]. The radiation polymerisation of *N*-vinylcarbazole[133,154,236,237], *N*-vinylcaprolactam[159,238], *N*-vinylsuccinimide[159,238-241], and *N*-vinylphthalimide[18] has been carried out in the liquid and solid phases. According to data obtained by thermal analysis, the last two monomers in the solid phase polymerise autocatalytically and explosively. For the solid-phase polymerisation and post-polymerisation of *N*-vinylsuccinimide, two alternatives have been observed, differing in their dependence on the temperature, dose rate, and dimensions of the specimen: that involving a uniform thermal polymerisation stage and that involving thermal explosion[160]. The rate of polymerisation of *N*-vinylcarbazole changes little on going from the solid phase to the liquid phase[237]. The polymerisation of *N*-vinylcaprolactam in the solid phase is very slow, whereas the process is rapid in the supercooled state[160]. *N*-Vinylpyridinium salts also polymerise under the influence of ^{60}Co γ-radiation in solution (water of dimethylformamide) and in the solid phase[242,243]. The polymers are amorphous and in aqueous solution have the properties of a polymeric electrolyte. It is suggested that the reaction in the liquid and solid phases takes place by a radical mechanism.

It should be emphasised that the polymerisation of this group of monomers involves the double bond of the vinyl group, the heterocycle being preserved.

8. ALLYL MONOMERS

Allyl derivatives, with the exception of allylsilanes and allyl hydrocarbons do not polymerise under ordinary conditions. Only a few form oligomers. In this case radiation initiation is the only means of obtaining polymers. The action of γ-radiation has made it possible to obtain macromolecular products from allyl alcohol, allyl chloride and bromide, allyl acetate, allyl ethyl ether, allylamine, allyl nitrile, and other monomers[28,244-246]. The polymerisation takes place by opening of the double carbon–carbon bond, but with allyl nitrile, the nitrile functional group also takes part. The radiation-chemical yield is low (up to 50 molecules per 100 eV). Despite the large doses used (up to 10^9 r g^{-1}), almost, no radiolysis of the monomers or cross-linking of the polymeric products takes place, however[28].

Allylidene diacetate polymerises when irradiated "in bulk".[247] The polymer

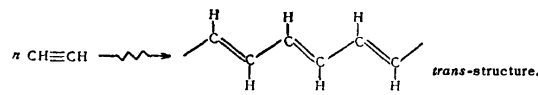


consists of a white powder with molecular weight up to 2750 and m.p. 130–140°; it is soluble in the monomer, acetone, benzene, and dioxan. It can be hydrolysed.

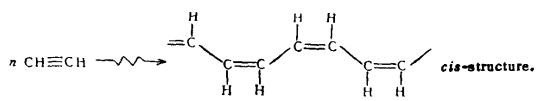
9. ALKYNE MONOMERS

The polymerisation of acetylene and its homologues gives polyvinylenes — structures with a conjugated system of double bonds. These substances have a high heat resistance and electrical conductivity.

The influence of α-radiation on gaseous acetylene was one of the first examples of radiation polymerisation to be observed. The resulting insoluble yellow powder is similar to cuprene, but subsequent electron-microscope study showed that it differs from cuprene and the name "alprene" was proposed for the product[248,249]. Benzene is formed in addition to the solid polymer ($G_{polymer}$ = 60 molecules per 100 eV and $G_{benzene}$ = 5.1 molecules per 100 eV). The polymerisation of acetylene also takes place under the influence of β-radiation from tritium[250]. Sensitisation of the polymerisation in gaseous medium by noble gases has been observed when α-radiation from radon[251,252] and X-rays[253,254] were used. The radiation polymerisation of acetylene in the liquid and solid phases has also been studied[208,210,255,256]. The possibility of formation of a polymer with regular structure has been noted (*trans*--configuration for irradiation of acetylene in the solid state):



trans-Polyacetylene is insoluble and is dark red. To explain the solid-phase polymerisation, the authors suggest an "electronic polymerisation" mechanism[257] (see Section 12 below). In the liquid phase, in the authors' opinion, the polymerisation takes place by a cationic mechanism with the formation of a *cis*-structure[256]:

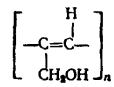


cis-Polyacetylene is soluble and brown.

Phenylacetylene polymerises under the influence of electrons (1.5 MeV) in an atmosphere of air and in a vacuum[258-262]. The value of G is low: 9 molecules per 100 eV. The number-average molecular weight of the polymer is 1100. Atmospheric oxygen accelerates the polymerisation and the yield increases by a factor of 1.5–2. Radiation poly(phenylacetylene)[260] is yellow--orange and soluble in acetone, benzene, esters, and carbon tetrachloride. It is insoluble in petroleum ether and alcohol. The purified product melts at 170–190°. Atmospheric oxygen does not influence the polymerisation of hex-1-yne and cyclohexylacetylene[259], unlike phenylacetylene.

The polymerisation of perfluorobut-2-yne (^{60}Co γ-radiation, dose rate 0.36 Mr h^{-1}, duration of irradiation 67 h) leads to the quantitative formation of a heat-resistant solid white polymer which is not attacked or even wetted by boiling concentrated sulphuric acid, concentrated nitric acid, or 50% sodium hydroxide solution. The polymer is

insoluble in ether, CCl_4, methanol, benzene, and other common solvents[263]. Thermographic analysis shows that its decomposition in nitrogen begins at 425° and that the point of 50% degradation is 75 deg higher than for poly(tetrafluoroethylene). The rate of polymerisation of prop-2-ynyl bromide and prop-2-ynyl alcohol is unaffected by the presence of air[261]. The prop-2-ynyl alcohol polymer is a dark red product with structural unit[208,210]:



Macromolecular products are obtained by the radiation polymerisation of 2,2-dimethyltrimethylene dipropiolate and acetylenedicarboxylic acid[264].

10. CARBONYL COMPOUNDS

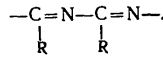
Characteristic features of the radiation polymerisation of aldehydes involving opening of the C=O bonds are the very high rates and the consequent use of extremely small doses. According to a patent taken out by a Japanese firm, anhydrous formaldehyde, emulsified at -16° in n-hexane solution, polymerises under the influence of ^{60}Co γ-radiation at a dose rate of 900 r h^{-1}.[265] According to another patent[266], absolutely anhydrous liquid formaldehyde (m.p. -118°) at -30° and -100° and high dose rates of 10^2–10^8 r h^{-1} forms a polymer which is more stable than that obtained by ordinary polymerisation. Under the influence of γ-rays and X-rays, the polymerisation in the solid phase[267–269] develops satisfactorily at temperatures from -75° to -196° at very small doses (less than 2000 r); this requires extremely low-power sources. Explosive polymerisation was observed at lower temperatures. The values of G are exceptionally high and amount to 5.4×10^6 molecules per 10 eV; $[\eta]$ for the polymer is 3.5–4.0.[269] Comparison of the polymerisation of acetaldehyde in the liquid[270,271] and solid[270,272,273] phases showed that, as for formaldehyde, the process takes place readily in the solid phase and the product is a rubber-like polymer with high molecular weight (up to 1.5 million). In the liquid phase a polymer with M = 140 000–500 000 is formed. No post-effect is observed. In the solid phase the radiation polymerisation takes place by a mechanism involving propagation through the crystal lattice[272]. Radiation polyacetaldehyde is apparently as unstable as the polymer obtained by ordinary polymerisation. Propionaldehyde at -196°, at a dose of 0.57 Mr and a dose rate of 4750 r × × min^{-1} (X-rays) gives an elastomer (degree of conversion 3%) extremely similar to radiation polyacetaldehyde[267,270,271]. The polymerisation of acrolein[274–276] "in bulk" gives an extensively cross-linked (by polymerisation at the C=C and C=O bonds) vitreous polymer insoluble in aqueous sulphuric acid solution. The rate of polymerisation is increased in solutions, particularly aqueous solutions. The product is a polymer which is soluble in sulphuric acid and contains reactive aldehyde groups[274]. The same effect is achieved by polymerisation "in bulk" at -78°.[276] Radiation polymerisation in aqueous medium leads to the formation of a water-insoluble polymer[277]. The γ-irradiation of chloral at a dose rate of 0.068 r h^{-1} at low temperatures gives a colourless solid polymer[278].

The γ-irradiation of dimethylformamide with ^{60}Co at low temperatures gives a polymer in the form of a reddish orange oil, immiscible with water[279]. The polymerisation apparently involves opening of the C=O bonds.

Acetone has been polymerised in the solid phase at -136° and -196° under the influence of γ-radiation[280]. The yield of polymer is 0.1–1% and G amounts to 30–500 molecules per 100 eV. The polymer is a yellow unstable elastomer. Data obtained by infrared spectroscopy indicate the presence of polyether units (–O–C–O–). Chloroacetone and bromoacetone have also been polymerised in the solid phase[280]. For chloroacetone at -78°, G = 8.4 molecules per 100 eV. For bromoacetone under the same conditions, G = 470 molecules per 100 eV. The polymerisation of methyl vinyl ketone "in bulk" at temperatures from 22° to -78° takes place by a radical mechanism with monomolecular termination[281].

11. NITRILES OF SATURATED CARBOXYLIC ACIDS

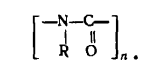
Polymerisation of nitriles at the triple bond should give hetero-chain polymers with a conjugated system of bonds



These polymers have a high heat-resistance and semiconductor properties[282]. The radiation polymerisation of acetonitrile[208,261,283] takes place by an anionic mechanism, as established by comparison of radiation polyacetonitrile with polymers obtained using cationic and anionic catalysts and by radical polymerisation. The polymers (dark brown adhesive or elastic products) are formed with low values of G (10–50 molecules per 100 eV). The degree of polymerisation is also low (~10–50). The acetonitrile polymer is soluble in the monomer and in dimethylformamide. The infrared spectrum of radiation polyacetonitrile indicates the presence of C=N–C=N and N=C=N bonds. According to data given in a patent[284], G for the polymerisation of acetonitrile at a dose of ~4.35 Mr and a dose rate of 0.0195 Mr h^{-1} has the values (molecules per 100 eV) 8.4 and 12.6 at 20° and -78° respectively. The radiation polymerisation of propionitrile, isobutyronitrile[208,283], and n-butyronitrile[208] in the solid phase has been observed. Experiments with the addition of ethylene showed that it acts as a sensitiser[208]. The results of the radiation polymerisation of propionitrile, butyronitrile, and benzonitrile in the liquid and solid phases[284] are analogous to the results obtained in the polymerisation of acetonitrile.

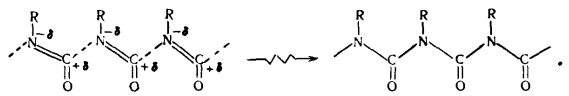
12. ISOCYANATES

It is suggested that in the radiation polymerisation of isocyanates[285,286], as in the case of "material" initiation, the polymers are formed by opening of the N=C bonds with units:



Methyl and phenyl isocyanates in the liquid and solid phases give amorphous polymers[286]. Polymethyl isocyanate is a white solid, melting with decomposition at 210°.[285] Butyl isocyanate forms an amorphous polymer in the liquid phase and a crystalline stereoregular polymer at low temperature in the solid phase[286]. The rate of polymerisation is much higher in the solid phase

than in the liquid phase. It is assumed that at low temperature with radiation initiation, stereospecific polymerisation takes place, as happens under analogous conditions for acrylonitrile, methacrylonitrile[208], and acetylene[208,255]. The process takes place by an anionic mechanism in the liquid phase. To explain the process taking place in the solid phase, the authors introduce the so-called "electronic" mechanism of polymerisation, with the assumption that here the process is neither ionic nor radical[286]. These ideas are essentially based on the concept previously put forward in principle by Semenov[287]. The Japanese authors emphasise the importance of the electronic state of the crystal as a whole at low temperature, pointing out the strong electronic interaction between the molecules of the monomer in the crystalline state:



From this examination of the electronic state, in the authors' opinion, it follows that the monomer in the crystal at low temperature is present in an excited state produced by the strong collective interaction. Under the influence of ionising radiation the ordered molecules give corresponding macromolecular compounds.

13. CYCLIC MONOMERS

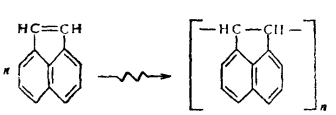
The polymerisation of this group of monomers is brought about either by opening of the ring or at an unsaturated bond in the ring.

Among the carbocyclic compounds, the aromatic hydrocarbons and acenaphthylene are noteworthy. The formation of polymers by the irradiation of benzene has been noted[288-291]. The value of G for the polymerisation is negligibly small (0.76 [288] or 0.91 [290]). The polymeric products are unsaturated yellow oils with M = 250–530. It has been suggested that the polymers are formed by opening of the benzene ring when benzene is irradiated in the liquid and solid phases[210,280]:

$$-CH=CH-CH=CH-CH=CH- \quad [210, 280].$$

As for benzene, irradiation of toluene produces a polymer with low radiation yield (0.92 molecules per 100 eV)[288]. The formation of a *p*-xylene polymer on irradiation in a reactor (yield 8%) has been noted[291]. Polynuclear aromatic hydrocarbons (biphenyl, terphenyl, etc.) are extremely stable to radiation and on prolonged irradiation form only traces of polymers[292]. Their stability to radiation increases and their tendency to polymerise decreases with increase in the number of aromatic rings in the molecule.

The polymerisation of acenaphthylene takes place under the influence of X-rays in the solid phase in an atmosphere of air or nitrogen and in a vacuum[293]:

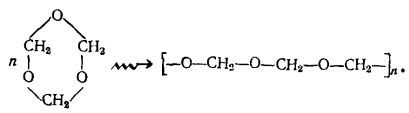


For irradiation in the liquid phase at 125° with a dose of 1.6 Mr the yield is 51.7%. The polymer is a white or yellow solid amorphous product with molecular weight 606 000. Thermal analysis shows no change in the polymer on heating in an atmosphere of air or nitrogen to 350°.

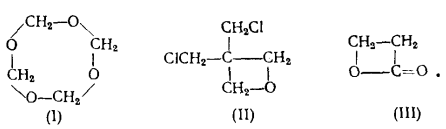
Study of the radiation polymerisation of heterocyclic compounds, particularly in the solid phase, has led to important results.

Sylvan (2-methylfuran) is relatively stable to radiation because of its conjugated system of double bonds: the pure monomer is not polymerised even at doses of 25 Mr.[294] The addition of 30–40 rel.% CCl_4 or $CHCl_3$ at doses above 5 Mr leads to the formation of resinous products (yield 70–80 wt.%) which are soluble in acetone and give lacquer coatings[294]. The formation of a polymer from furfuryl alcohol under the influence of ^{60}Co γ-rays has been reported[295].

Trioxan (m.p. 62°) polymerises readily in the solid state under the influence of γ-radiation or electrons with the formation of poly(oxymethylene)[296-302]:



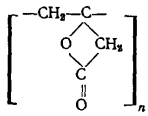
At a dose of 0.44 Mr for polymerisation in the liquid phase at 80° the yield of polymer is ~ 1%, whereas in the solid phase it increases to 16% at 50° and to 22% at 55°.[19] The degree of conversion of the monomer increases when it is subjected to high pressure before irradiation[302]. The polymerisation takes place more readily in large single crystals than in fine crystals[296] and the polymers have a higher melting point (198° and 186° respectively)[303]. The post-polymerisation has been noted and studied[302,304-306]. Radiation poly(oxymethylene) prepared from trioxan has a higher melting point and better heat resistance than the polymer from formaldehyde[297]. Microscope studies show that this product, like the radiation polymers from 3,3-bischloromethyloxacyclobutane, β-propiolactone, and diketen described below, can be obtained in the form of fibres. The sulphur-containing analogue of trioxan — trithian — forms polythioformaldehyde under the influence of γ-radiation at room temperature at doses up to 10 Mrad with subsequent heating at 180° (35 deg below the melting point of trithian)[307-309]. Tetraoxan (tetraoxymethylene) (I) (m.p. 120°) in the form of single crystals was exposed to ^{60}Co γ-radiation at a dose of 0.45 Mr at 80° and gave poly(oxymethylene) in 94% yield[310,311].



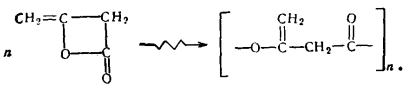
(I) (II) (III)

3,3-Bischloromethyloxacyclobutane (3,3-bischloromethyloxetan) (II) — the monomer of "Penton" — forms a polymer with linear structure[296,297,312]. The yield is greater from a large single crystal than from fine crystals[296,297]. Post-polymerisation has been noted[304,312]. The monomer polymerises only in the solid state (from 16° to -78°). The melting point of the polymer is 171–176°, that is 8–10 deg higher than for polymerisation with BF_3.[313] The solid-phase polymerisation of 3,3-bisbromomethyloxacyclobutane and 3,3-bisiodomethyloxacyclobutane has also been studied. The chlorine-containing monomer is the most reactive and the reactivity of the iodine derivative is very low (Cl > Br ≫ I).[314]

Of the lactones, β-propiolactone (III) polymerises in the solid phase with opening of the ring under the influence of γ-rays and electrons. The yield at -78°, a dose of 143 000 r, and a dose rate of 9000 r h^{-1} is 13.2% from a large single crystal and 10.9% from fine crystals[296,297]. Data characterising the kinetics of polymerisation indicate an ionic mechanism[315]. The polymer obtained from single crystals shows a high orientation of the crystalline regions[303,310]; its crystallinity and melting point are higher than those of the polymer obtained by ordinary polymerisation with ionic catalysts. With chemical initiation, diketen is capable of polymerising either at the $CH_2=C<$ bond in the case of radical initiation with the formation of a polymer of the vinyl type



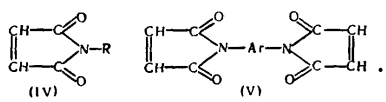
or with opening of the ring under the influence of ionic catalysts with the formation of polymeric products of the ester type. In radiation polymerisation in the solid state, a polymer of the polyester type is formed[296,297]:



The radiation polymer has a higher melting point and better crystallinity than the polymers obtained using ionic catalysts[297].

Maleic anhydride polymerises under the influence of ^{60}Co γ-radiation "in bulk" and in solution in benzene and acetic anhydride. In the latter at a dose of 40 Mr and a dose rate of 0.195 Mr h^{-1} the degree of conversion reaches 90%.[27] The polymerisation apparently involves opening of the double carbon–carbon bond in the ring.

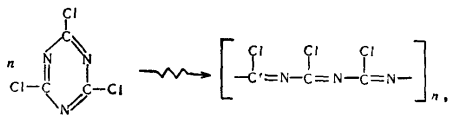
The imides of maleic acid (maleimides) polymerise readily in the solid phase. Studies have been made of the polymerisation, under the influence of ^{60}Co γ-radiation, of various *N*-substituted monomaleimides (IV) and dimaleimides (V):



(IV) (V)

N-phenylmaleimide[316–320], *N*-*p*-tolylmaleimide, *N*-2,4-dimethylphenylmaleimide, *N*-benzylmaleimide[320], *N*-carbamylmaleimide[320,321], *NN'*-*p*-phenylenedimaleimide, and *NN'*-4,4'-biphenylylenedimaleimide[322,323]. The degree of conversion is high close to the melting point of the monomers, for example up to 95% at a dose of up to 3 Mrad for *N*-*p*-tolylmaleimide[320]. The solid-phase polymerisation at 20° is sensitised by solid trichloroacetic acid[318–320] and liquid trifluoroacetic acid[320]. The monomaleimides form soluble polymers[316–321] with softening temperatures from 168° for *N*-benzylmaleimide to 330° for *N*-2,4-dimethylphenylmaleimide[320]. Polymerisation takes place at the C=C bonds with preservation of the imide rings in the chain[318–320]. The dimaleimides form heat-resistant insoluble polymers[322,323].

The triazine derivative cyanuric chloride (the chloride of cyanuric acid), a crystalline substance with m.p. 154°,



is polymerised in the solid phase under the influence of γ-radiation[324]. The yield of polymer is 70% at 16°, a dose rate of 0.03 Mr h^{-1}, and a dose of 14 Mr. Opening of the triazine ring was confirmed by infrared spectroscopy. The polymer is soluble in dimethylformamide and does not melt below 260°.

Of the heterocyclic spiro-compounds, dioxaspiro-[3,3]heptane has been studied. It polymerises in the solid phase with the formation of an amorphous, insoluble, and infusible polymer, but the rate of polymerisation is lower than in the case of trioxan and 3,3-bischloromethyloxetane. Air sensitises the polymerisation under the beam and the post-effect[325].

14. ORGANOELEMENTAL MONOMERS

These monomers can in turn be divided into cyclic, vinyl, and allyl monomers. The formation of the macromolecular chains is here analogous to that for the corresponding groups of monomers previously examined.

Hexamethylcyclotrisiloxane polymerises in the solid phase under the influence of fast electrons (800 keV)[326] or ^{60}Co γ-radiation[327] by different mechanisms corresponding to its two crystalline modifications[328]. The polymerisation product at doses below 0.5 Mr, a dose rate of 0.05–0.25 Mr h^{-1}, and a temperature of 40° is a soluble polymer, whose infrared spectrum is analogous to that of linear polysiloxane[327]. It is suggested that the polymerisation takes place with opening of the ring according to an ionic mechanism, since this monomer is not polymerised with radical initiators[327]. The post-polymerisation has been studied[306]. Octamethylcyclotetrasiloxane polymerises in a very narrow temperature range in the solid phase close to the melting point of the monomer[329,330]. Heptamethylvinylcyclotetrasiloxane is polymerised in the liquid and solid phases. The polymerisation in the latter takes place at the vinyl groups to give fibrous polymers soluble in benzene[331]. The radiation polymerisation of allyldiethylsilane, allylethylphenylsilane, allyldiphenylsilane, diallylethylsilane, and triallylsilane has been studied[332,333]. The ease of polymerisation increases in the order given, due to the increase in the number of allyl groups and in the monoallylsilanes the activity of the monomers increases with the introduction of phenyl groups into the molecules. The polymerisation takes place at the double bond of the allyl group by a radical mechanism. Di- and tri-allylsilanes form cross-linked products by polymerisation "in bulk"; polymerisation of diallylsilanes in 20% benzene solution gives soluble polymers[334]. The latter are also obtained from the divinyl-derivatives[335,336] and trivinyl-derivatives[336,337].

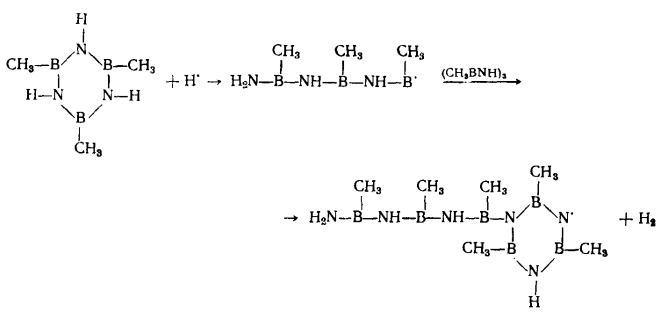
The radiation polymerisation of diethylvinylphosphine oxide and diphenylvinylphosphine oxide gives polymers with molecular weight 30 000–60 000 in

80–90% yield[338–340]. The molecular weight of the polymers obtained from these monomers by usual polymerisation methods does not exceed 3000–4000.

The study of the solid-phase polymerisation of the two polymorphic modifications of tributylvinylphosphonium bromide is of interest[341]. Under the influence of X-rays at temperatures from 30° to -80° and a dose rate of 0.28 Mrad h^{-1}, the radiation yield for 50% conversion varied in the range (molecules of monomer per 100 eV) 1147–9872, depending on temperature. An unusual effect was shown by atmospheric oxygen, which inhibits the polymerisation at 30° and -80° but sensitises the polymerisation at 0°. The polymer is amorphous, soluble in water, and hygroscopic. Its weight-average molecular weight is 50 000–96 000, glass point 5–16°, and heat resistance 340–396° (in air) or 396–411° (in nitrogen). Tributylvinylphosphonium iodide also polymerises in the solid phase under the influence of X-rays[342].

The radiation polymerisation of vinylsulphonamide has been studied in the liquid and solid phases[343,344]. The process is extremely rapid: at a dose rate of 0.25 Mr h^{-1} and 22° the rate of conversion of the monomer amounts to 75% h^{-1}, whereas for other monomers the rate is 1–17% h^{-1}.

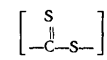
Among the organoboron monomers, the polymerisation of the borazoles has been studied. *BB'B"*-Trimethylborazole was irradiated in an electron accelerator (800 keV) and in an X-ray apparatus (800 kV, 200 mA)[345]. The polymer is a transparent resin with a low degree of polymerisation, readily soluble in benzene. A scheme of polymer formation by a radical mechanism has been proposed. The authors assume the formation of linear macromolecules from borazole rings and in some instances opening of the rings to form linear units, which may alternate with the rings in the chain:



BB'B"-Triphenylborazole and *BB'B"*-triphenyl-*NN'N"*-trimethylborazole (the latter on irradiation in the solid phase) form polymers which are insoluble in benzene but soluble in cresol. The polymers are brown powders which do not melt up to 300°.[345] Analogous polymerisation is undergone by the phosphorus-containing analogue of borazole — the cyclic dimethylphosphineborine trimer. The molecular weight of the polymer is 5200.[346]

15. INORGANIC MONOMERS

The polymer of dichlorophosphazene or so-called "inorganic rubber" has high heat resistance. With irradiation by electrons (4 MeV) the cyclic oligomers of dichlorophosphazene are more stable; the oligomers with an open chain polymerise more readily[347]. The polymerisation of the trimer has been described; in an electron accelerator (1–1.2 MeV) in an atmosphere of air at 130° the trimer can be completely polymerised to a sticky rubber-like mass containing a trace of the tetramer[348]. In the polymerisation of dichlorophosphazene in the solid phase at 100° under the influence of X-rays (dose rate 1.2 Mr h^{-1}) a degree of conversion of 10% is reached in 40 h.[349] The tetramer does not polymerise under the influence of γ-radiation either in the solid or in the liquid phase[350]. On irradiation of the trimer in the solid phase the rate of polymerisation increases with increase in temperature to the melting point but above this temperature it decreases to almost zero[350]. In the polymerisation of dicyan (cyanogen) $(CN)_2$ from the gaseous phase, it was found that argon, krypton[253], and xenon[253,351] have a sensitising influence. Analogous studies were carried out with hydrogen cyanide[253]. A carbon disulphide polymer was previously obtained by thermal polymerisation at 185° and a pressure of about 55 000 atm[352]. Infrared spectroscopy indicated that the solid black polymer had the microstructure



The action of ^{60}Co γ-radiation gives a brown product at a pressure of 1 atm and a black product at high pressures (up to 15 000 atm). The polymer is insoluble in the monomer but swells in it. The yields of polymer are very low. The maximum yield of 4.1% (G = 1.5) was obtained at a dose of 400 Mr, a dose rate of 3.2 Mr h^{-1}, a temperature of 98° and a pressure of 10 000 atm.[120,352] It is reported that carbon monoxide forms a polymer under the influence of ionising radiation[34].

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PRINCIPLES OF THE PREPARATION OF BUTADIENE BY THE DEHYDROGENATION OF BUTANE AND BUTENE

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1. INTRODUCTION

The annual world production of buta-1,3-diene (divinyl), the most important monomer for the synthesis of many types of rubber, has long exceeded one million tons; the greater part of the butadiene is at present obtained by the catalytic dehydrogenation of n-butane and n-butene[1].

As a result of studies of the catalytic dehydrogenation of butane and butene, begun as early as the nineteen-thirties in the USSR and other countries, large factories were constructed in the USA during the Second World War for the production of butadiene by the single-stage dehydrogenation of butane in a vacuum, by the dehydrogenation of butene in the presence of water vapour†, and also by the two-stage dehydrogenation of butane according to the scheme: butane → butene → butadiene[1]. In the post-war years, several synthetic rubber factories were constructed in the USSR for the production of butadiene by the two-stage dehydrogenation of butane.

Because of their great practical importance, the dehydrogenation processes have been studied for many years in this country and abroad. The aim of studies of the dehydrogenation reactions is not limited to the solution of applied problems, however; the results of these studies have made an important contribution to the theory of heterogeneous catalysis. In particular, Balandin's multiplet theory of catalysis was developed in a study of the mechanism and kinetics of dehydrogenation reactions.

The number of papers devoted to the study of the dehydrogenation of hydrocarbons amounts to several hundred. The most detailed reviews are those of Kearby[2] and Lyubarskii[3]; the first of these covers the literature up to 1953, gives the equilibrium degrees of dehydrogenation at different temperatures, and describes industrial catalysts and methods of dehydrogenation; the second covers the literature up to 1957, describes in considerable detail the results of the development of catalysts for the dehydrogenation of alkanes, and gives data on the rate of dehydrogenation of butane, butene, and isopentane, obtained in the Karpov Physicochemical Institute.

The aim of the present paper is to review the accumulated material on the chemistry of the reactions taking place in the catalytic dehydrogenation of butane and butene, and on the equilibria and kinetics of these reactions.

2. REACTIONS TAKING PLACE IN THE DEHYDROGENATION OF BUTANE AND BUTENE

In the catalytic dehydrogenation, many side reactions take place in addition to the main reactions involving the conversion of butane into butene and of butene into butadiene[4-6].

1. The main reactions are evidently:

$$n\text{-}C_4H_{10} \rightleftharpoons CH_3.CH_2.CH{=}CH_2 + H_2, \quad (1a)$$

$$n\text{-}C_4H_{10} \rightleftharpoons cis\text{-}MeCH{=}CHMe + H_2, \quad (1b)$$

$$n\text{-}C_4H_{10} \rightleftharpoons trans\text{-}MeCH{=}CHMe + H_2, \quad (1c)$$

or, overall,

$$n\text{-}C_4H_{10} \rightleftarrows n\text{-}C_4H_8 + H_2, \quad (1)$$

where $n\text{-}C_4H_8$ represents the equilibrium mixture of n-butene isomers;

$$EtCH{=}CH_2 \rightleftharpoons C_4H_6 + H_2, \quad (2a)$$

$$cis\text{-}MeCH{=}CHMe \rightleftharpoons C_4H_6 + H_2, \quad (2b)$$

$$trans\text{-}MeCH{=}CHMe \rightleftharpoons C_4H_6 + H_2, \quad (2c)$$

or, overall,

$$n\text{-}C_4H_8 \rightleftarrows C_4H_6 + H_2. \quad (2)$$

Let us now examine the side reactions.

2. The cracking of $n\text{-}C_4H_{10}$ in general cannot be described by a single stoichiometric equation, since the stoichiometric coefficients (and possibly even the composition of the reaction products) may depend on the temperature, degree of decomposition, and type of catalyst; these problems have been little discussed in the literature, however. It is stated[7] that the thermal cracking of $n\text{-}C_4H_{10}$ at 520°C and a degree of transformation up to 25% is described by the following reactions, which can be regarded as primary reactions:

$$15\ n\text{-}C_4H_{10} \rightarrow 10\ C_3H_6 + 10\ CH_4, \quad (3a)$$

$$\rightarrow 4\ C_2H_4 + 4\ C_2H_6, \quad (3b)$$

$$\rightarrow n\text{-}C_4H_8 + H_2, \quad (3c)$$

(that is, $15n\text{-}C_4H_{10} \rightarrow 10C_3H_6 + 10CH_4 + 4C_2H_4 + 4C_2H_6 + n\text{-}C_4H_8 + H_2$).

3. The cracking of $n\text{-}C_4H_{10}$ during its catalytic dehydrogenation to butene on one of the catalysts[5] takes place according to the equation

$$n\text{-}C_4H_{10} \rightarrow 0.12H_2 + 0.49CH_4 + 0.39C_2H_4 + 0.38C_2H_6 + 0.49C_3H_6 + 0.01C_3H_8 + 0.12C_4H_8, \quad (3d)$$

but on the catalyst used in the USSR it is described approximately by the equation[6]

$$n\text{-}C_4H_{10} \rightarrow 0.62CH_4 + 0.13C_2H_4 + 0.44C_2H_6 + 0.04C_3H_6 + 0.2C_3H_8 + 0.3(C_5+). \quad (3e)$$

† The use of water vapour achieves three results: the partial pressure of $n\text{-}C_4H_8$ is reduced, displacing the equilibrium towards the formation of C_4H_6, the necessary heat is supplied, and the deposited "carbon" is removed.

4. The cracking of $n\text{-}C_4H_8$. A characteristic feature of the primary reactions involved in the thermal cracking of $n\text{-}C_4H_8$ is their much greater variety. Analysis of published data[8-14] indicates that at temperatures up to 600°C and small degrees of transformation in the thermal decomposition of but-1-ene and but-2-ene, the products are H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_6, and liquid hydrocarbons. The highest thermal stability is shown by but-2-ene.[13] The following can be regarded as the primary reactions in the thermal decomposition of $n\text{-}C_4H_8$:

$$n\text{-}C_4H_8 \rightleftarrows C_4H_6 + H_2, \quad (4a)$$
$$n\text{-}C_4H_8 + H_2 \rightarrow C_2H_4 + C_2H_6, \quad (4b)$$
$$n\text{-}C_4H_8 \rightarrow 2\,C_2H_4, \quad (4c)$$
$$n\text{-}C_4H_8 + H_2 \rightarrow CH_4 + C_3H_6, \quad (4d)$$
$$3n\text{-}C_4H_8 \rightarrow CH_4 + C_3H_6 + C_8H_{14}. \quad (4e)$$

The greater part of the $n\text{-}C_4H_8$ decomposes according to reaction (4d). It is suggested[5] that the cracking of $n\text{-}C_4H_8$ in its dehydrogenation on one of the catalysts (in the presence of water vapour) takes place according to the equation

$$n\text{-}C_4H_8 \rightarrow 0.25H_2 + 0.27CH_4 + 0.15C_2H_4 + 0.31C_3H_6 + 0.5C_4H_6 + 0.08 + 0.08(C_5+) + 0.1C. \quad (4)$$

5. Transformation of butadiene. The main reaction of C_4H_6 at 400–700°C and atmospheric pressure is its dimerisation[15] and this reaction is apparently the primary reaction:

$$2\,C_4H_6 \rightleftarrows C_8H_{12}. \quad (5a)$$

In the presence of dehydrogenation catalysts, this reaction is accompanied by the decomposition of butadiene (or its dimer) with the formation of lighter hydrocarbons and carbonaceous deposits ("carbon"); the following equations were found for two different catalysts for the dehydrogenation of $n\text{-}C_4H_8$:

According to the data of Beckberger and Watson[5]

$$C_4H_6 \rightarrow 0.56CH_4 + 0.07C_2H_4 + 0.58C_3H_6 + 1.49C, \quad (5b)$$

according to our data[16]

$$C_4H_6 \rightarrow 0.098CH_4 + 0.024C_2H_4 + 0.017C_3H_6 + 0.68C_4H_8 + 1.08C. \quad (5c)$$

The last equation was obtained[16] on the basis of the composition of the products of the decomposition of C_4H_6 on passage over a catalyst at 560–600°C and molar ratio $C_4H_6 : H_2O = 1 : 10–1 : 30$.

6. Isomerisation of $n\text{-}C_4H_{10}$ and $n\text{-}C_4H_8$. The following reactions are observed in the catalytic dehydrogenation

$$n\text{-}C_4H_{10} \rightleftharpoons iso\text{-}C_4H_{10}, \quad (6a)$$
$$n\text{-}C_4H_8 \rightleftharpoons iso\text{-}C_4H_8. \quad (6b)$$

7. Reactions of water vapour. In the dehydrogenation of butene in the presence of water vapour (the usual industrial conditions) the "carbon" formed on the catalyst — for example, according to reactions (5b) or (5c) — reacts with water vapour. It is assumed[17] that the following reactions take place in the interaction between water vapour and carbon (in particular during its gasification):

$$C + H_2O \rightleftarrows CO + H_2, \quad (7a)$$
$$C + 2H_2O \rightleftarrows CO_2 + H_2, \quad (7b)$$
$$CO_2 + H_2 \rightleftarrows CO + H_2O, \quad (7c)$$
$$C + 2H_2 \rightarrow CH_4, \quad (7d)$$

and a number of others. Two generally similar equations have been given for the reaction of water vapour with "carbon" deposited in the catalytic dehydrogenation of $n\text{-}C_4H_8$; one of these is[5]

$$H_2O + 0.512C \rightarrow 0.488CO_2 + 0.024CO + H_2, \quad (7e)$$

and the other is[16]

$$H_2O + 0.5068C \rightarrow 0.4931CO_2 + 0.0137CO + H_2. \quad (7f)$$

8. Reduction of the oxides of the catalyst. As shown below, many of the catalysts used in industry for the dehydrogenation of butane and butene contain the oxides of metals with variable valency — chromium and iron. The higher-valency oxides formed during their regeneration, that is, in the high-temperature calcination in a current of oxygen-containing gas, are converted into lower-valency oxides during the dehydrogenation in a reducing medium. For example[18],

$$CrO_3 \xrightarrow{C_nH_m} Cr_2O_3 + H_2O + CO_2 + CO,$$

and similarly for iron oxide

$$Fe_2O_3 \xrightarrow{C_nH_m} Fe_3O_4 \rightarrow FeO + H_2O + CO_2 + CO$$

Reduction may also be brought about by the hydrogen formed in the dehydrogenation, but analysis of the products[18,19] indicates that, for example, the CrO_3 in the aluminium–chromium catalyst is reduced chiefly by hydrocarbons. Other views have been put forward regarding the chemistry of the reduction of aluminium–chromium catalysts (with added potassium oxide); for example, it is suggested[20] that K_2CrO_4 is formed in the regeneration and that the following reaction takes place during dehydrogenation

$$2\,K_2CrO_4 + 2\,Al_2O_3 \xrightarrow{H_2} 4\,AlOOK + Cr_2O_3 + H_2O.$$

9. Reactions during the regeneration of the catalysts. The chief reactions in the regeneration of dehydrogenation catalysts are the combustion of the carbonaceous deposits and the change of the oxides of the catalysts from a lower valency to a higher valency. In particular, it has been shown[18,21-25] that in the regeneration of chromium and aluminium–chromium catalysts, Cr_2O_3 is converted into CrO_3; in addition, solid solutions of oxygen in chromium oxide may be formed.

10. Reactions leading to the formation of carbonaceous deposits. Important reactions in the dehydrogenation of butane and butene are those leading to the formation of carbonaceous deposits, which contain an appreciable quantity of hydrogen in addition to carbon[26] and which would be more correctly called tarry deposits. There are grounds for assuming[6,26-28] (the nature of the change in the composition of the carbonaceous deposits with change in the dehydrogenation conditions, and the formation of benzene, toluene, styrene, and other aromatic and cyclic hydrocarbons as side-products) that the so-called "carbon" deposited on the catalyst is formed not according to reactions (5b) or (5c) but according to the scheme:

$2C_4H_6 \rightarrow$ (vinylcyclohexene) $\rightarrow$ ... (polycondensation, dehydrogenation, cracking) ... $\rightarrow$ polycyclic hydrocarbons $\rightarrow$ ("tars" or "carbons").

11. Other reactions. The above list does not exhaust all the reactions taking place in the dehydrogenation of butane and butene, but these are the most important[6]. Other reactions which evidently take place in the dehydrogenation of n-C_4H_{10} and n-C_4H_8 are the dehydrogenation of the iso-C_4H_{10} formed by the isomerisation of n-C_4H_{10}, and the cracking of iso-C_4H_{10} and iso-C_4H_8, but the part played by these reactions is slight.

3. REACTION EQUILIBRIA

The equilibrium constant for the chemical reaction is calculated from the familiar equation

$$RT\ln K_{pT} = -\Delta G^\circ_T = -\Delta H^\circ_T + T\Delta S^\circ_T,$$

and the degree of transformation x is related to K_p by an equation which depends on the form of the stoichiometric equation for the reaction. Methods for calculating the thermodynamic quantities and their values at different temperatures have been described in a number of familiar works[29-32], so that here we shall give for most reactions only the final equations for calculating the values of $\log K_p$ and the necessary data confirming the applicability of these equations; for some reactions we shall give the most reliable tabulated data.

1. The reaction n-$C_4H_{10} \rightleftarrows$ n-$C_4H_8 + H_2$. The experimental and calculated data on the equilibrium for the dehydrogenation reaction have been reviewed[29].

Comparison of the values of K_p and x calculated on the one hand[2,6] from the latest and now generally accepted thermodynamic data, and on the other hand[6] from the empirical equations proposed by various authors, shows that the most satisfactory equations are those of Korobov and Frost[33]:

$$\begin{aligned}\log K_{p_1-a} &= \frac{-6586}{T} + 6.685,\\ \log K_{p_1-b} &= \frac{-6209}{T} + 6.639,\\ \log K_{p_1-c} &= \frac{-5992}{T} + 6.112.\end{aligned} \qquad (1)$$

The equilibrium constant for the overall reaction (1) is:

$$K_{p_1} = K_{p_1-a} + K_{p_1-b} + K_{p_1-c},$$

and the degree of transformation is

$$x_1 = \left(\frac{K_{p_1}}{K_{p_1} + P_{total}}\right)^{0.5}.$$

In the range 760–900°K, more accurate values of K_{p_1} are obtained from the equation[6]:

$$\log K_{p_1} = \frac{-30\,500}{4.575T} + 7.574. \qquad (2)$$

The values of K_p and x_1 calculated from Eqns. (1) and (2) are compared in Table 1 with the calculated values obtained[2] from thermodynamic data[32].

When side reactions take place simultaneously, the equilibrium degrees of dehydrogenation will differ from the values given in Table 1. When only the reaction $C_4H_{10} \rightleftarrows C_4H_8 + H_2$ takes place and the degree of dehydrogenation is x_1, the partial pressures of the components are:

$$P_{C_4H_{10}} = \frac{1-x_1}{1+x_1}P_{total}, \qquad P_{C_4H_8} = P_{H_2} = \frac{x}{1+x}P_{total}.$$

TABLE 1. Equilibrium constants and equilibrium extents to which reaction (1) takes place at $P_{total} = 1$ atm.

T, °K	According to Eqn. (1)		According to Eqn. (2)		Calculations from thermodynamic data (Ref. 32)	
	K_{p_1}	x_1	K_{p_1}	x_1	K_{p_1}	x_1
760	0.0563	0.231	0.057	0.23	0.063	0.235
780	0.0945	0.296	0.106	0.31	0.105	0.309
800	0.1454	0.356	1.179	0.39	0.174	0.389
820	0.2258	0.433	0.282	0.47	0.282	0.47
840	0.3403	0.504	0.429	0.55	0.429	0.55
860	0.5069	0.580	0.667	0.63	0.667	0.63
880	0.7407	0.652	1.00	0.71	1.00	0.71
900	1.063	0.720	1.630	0.79	1.480	0.78

Substituting these values in the equation $K_{p_1} = \frac{P_{C_4H_8}P_{H_2}}{P_{C_4H_{10}}}$, we obtain

$$x_1 = \left(\frac{K_{p_1}}{K_{p_1} + P_{total}}\right)^{0.5}.$$

When side-reactions take place, the total number of reaction products is not $1 + x_1$ but α_1; since some of the n-C_4H_8 formed is used up in secondary reactions, the number of moles of n-C_4H_8 becomes equal to $x_1\gamma_1$ (where γ_1 is the selectivity of the dehydrogenation), and the quantity of hydrogen increases to $x_1\gamma_1\beta_1$, where β_1 is a coefficient for the excess of hydrogen, equal to $P_{H_2}/P_{C_4H_8}$. Substituting these values in the equation for the equilibrium constant, we obtain

$$x_1 = \frac{-K_{p_1}\alpha_1 + \sqrt{K_{p_1}\alpha_1(4\gamma_1^2\beta_1 P_{total} + K_{p_1}\alpha_1)}}{2\gamma_1^2\beta_1 P_{total}}.$$

2. The reaction n-$C_4H_8 \rightleftarrows C_4H_6 + H_2$. Fairly accurate values of K_{p_2} and x_2 can be found from the equations[5]

$$\log K_{p_2} = \frac{-28\,000}{4.575T} + 5.70121, \qquad (3)$$

or[6]

$$\log K_{p_2} = \frac{-30\,500}{4.575T} + 6.33, \qquad (4)$$

as can be seen from Table 2, which gives the values of K_{p_2} and x_2, calculated[6] from these equations and found[2] from thermodynamic data[32].

The equation giving the dependence of x on K_p shows that with decrease in the total pressure (on dilution with an inert gas) the equilibrium degrees of dehydrogenation of butane and butene increase; the influence of reduced pressure is shown below for reaction (2):

	$P = 1$ atm						
T, °K	800	820	840	860	880	900	920
x_2	0.10	0.127	0.158	0.194	0.234	0.28	0.329
	$P = 0.1$ atm						
x_2	0.304	0.375	0.45	0.53	0.608	0.678	0.74
	$P = 0.05$ atm						
x_2	0.41	0.496	0.582	0.663	0.734	0.793	0.84

TABLE 2. Equilibrium constants and equilibrium extents to which reaction (2) takes place at P_{total} = 1 atm.

T, °K	According to Eqn. (3)		According to Eqn. (4)		Calculations (Ref. 2) according to published data (Ref. 32)	
	K_{p_2}	x_2	K_{p_2}	x_2	K_{p_2}	x_2
800	0.0112	0.106	0.00971	0.092	0.0102	0.10
820	0.0174	0.131	0.0159	0.124	0.0164	0.127
840	0.0263	0.159	0.0248	0.155	0.0256	0.158
860	0.0380	0.189	0.0378	0.19	0.0392	0.194
880	0.0550	0.229	0.0567	0.231	0.0585	0.234
900	0.0776	0.268	0.0838	0.278	0.0855	0.280
920	0.1096	0.307	0.121	0.32	0.1222	0.329

The equilibrium degree of dehydrogenation with allowance for side-reactions‡ is here equal to[6]:

$$x_2 = \frac{-K_{p_2}(\lambda+\alpha_2)+\sqrt{K_{p_2}^2(\lambda+\alpha_2)^2+4K_{p_2}(\lambda+\alpha_2)(P_{total}\gamma_2^2\beta_2)}}{2\gamma_2^2\beta_2 P_{total}}.$$

Equilibrium for the Dehydrogenation of Butane-Butene Mixtures. In the single-stage method for the preparation of butadiene, a butane–butene mixture is dehydrogenated (at reduced pressure). The term "single-stage" is a technological description (the process takes place in a single reaction vessel and only n-C_4H_{10} is used up), but in actual fact the reaction takes place[34] according to the scheme

$$\text{n-}C_4H_{10} \rightarrow \text{n-}C_4H_8 \rightarrow C_4H_6.$$

The equilibrium degrees of dehydrogenation of a n-C_4H_{10} + n-C_4H_8 mixture in the presence of an inert diluent were first calculated by Bogdanov[35]. The calculation of the equilibrium composition in the dehydrogenation of n-C_4H_{10} + n-C_4H_8 at reduced pressure can be approached as follows[6]. Let us assume that n-C_5H_{10} : n-C_4H_8 = m : n and that $m + n = 1$. Let y_1 and y_2 be the numbers of moles of n-C_4H_8 and C_4H_6 formed. The equilibrium mixture will then contain the following numbers of moles:

$$\text{n-}C_4H_{10} = m - y_1;\ \text{n-}C_4H_8 = n + y_1 - y_2;\ C_4H_6 = y_2;\ H_2 = y_1 + y_2,$$

and a total of $1 + y_1 + y_2$ moles.

The partial pressures are

$$P_{C_4H_{10}} = \frac{m-y_1}{1+y_1+y_2}P_{total};\quad P_{C_4H_8} = \frac{n+y_1-y_2}{1+y_1+y_2}P_{total};$$

$$P_{C_4H_6} = \frac{y_2}{1+y_1+y_2}P_{total};\quad P_{H_2} = \frac{y_1+y_2}{1+y_1+y_2}P_{total}.$$

‡ $\lambda = H_2O/C_4H_8$ mole mole^{-1}.

The equilibrium constant for the reaction

$$\text{n-}C_4H_{10} \rightleftharpoons \text{n-}C_4H_8 + H_2,$$

is

$$K_{p_1} = \frac{(n+y_1-y_2)(y_1+y_2)}{(1+y_1+y_2)(m-y_1)}P_{total},$$

and the equilibrium constant for the reaction

$$\text{n-}C_4H_8 \rightleftarrows C_4H_6 + H_2,$$

is

$$K_{p_2} = \frac{(y_1+y_2)y_2}{(1+y_1+y_2)(n+y_1-y_2)}P_{total}.$$

Dividing the first equation by the second and introducing the symbols $\frac{n+y_1}{y_2} = a$ and $\frac{1}{y_2} = b$, we obtain

$$b = \frac{(1+a)P_{total}-K_{p_2}(a^2-1)}{K_{p_2}m(a-1)+nP_{total}}, \quad (5)$$

$$b = \frac{K_{p_2}(a-1)^2}{K_{p_1}} + a. \quad (6)$$

This system can be solved graphically. For this purpose, Eqn. (6) is used to construct curves giving the dependence of b on a for different temperatures; points are plotted on the resulting graph in accordance with Eqn. (5) (separately for each temperature and pressure). The equilibrium compositions calculated[6] in this way for the dehydrogenation of a n-C_4H_{10} + n-C_4H_8 mixture are given in Table 3.

Thus industrially acceptable yields of butadiene can be achieved at a temperature above 570°C and a pressure less than 125 mmHg at a concentration of n-C_4H_8 in the original mixture not less than 30%.

3. Cracking of n-C_4H_{10}. The results of calculations[36] of the equilibrium composition of the products obtained when only the primary reactions (3a)–(3c) take place indicate that under the conditions of dehydrogenation of n-C_4H_{10} (500–600°C) its equilibrium degree of cracking amounts to about 70–75%.

TABLE 3. Equilibrium n-C_4H_{10} + n-C_4H_8 + C_4H_6 composition for dehydrogenation of n-C_4H_{10} + n-C_4H_8 mixture.

Original n-C_4H_{10} + + n-C_4H_8 mixture	T, °K	P_{total} = 760 mmHg			250 mmHg			125 mmHg			95 mmHg		
		n-C_4H_{10}	n-C_4H_8	C_4H_6	n-C_4H_{10}	n-C_4H_8	C_4H_6	n-C_4H_{10}	n-C_4H_8	C_4H_6	n-C_4H_{10}	n-C_4H_8	C_4H_6
100:0	830	0.468	0.508	0.024	0.226	0.676	0.098	0.122	0.704	0.174	0.094	0.698	0.208
	850	0.378	0.58	0.042	0.162	0.698	0.14	0.082	0.673	0.245	0.063	0.643	0.294
	870	0.306	0.626	0.068	0.117	0.692	0.191	0.057	0.619	0.324	0.046	0.572	0.382
	890	0.246	0.649	0.105	0.088	0.66	0.252	0.044	0.542	0.414	0.035	0.492	0.472
80:20	830	0.404	0.561	0.035	0.213	0.678	0.109	0.128	0.685	0.186	0.104	0.681	0.215
	850	0.33	0.617	0.053	0.158	0.691	0.151	0.194	0.653	0.253	0.073	0 630	0.297
	870	0.279	0.642	0.079	0.12	0.68	0.20	0.07	0.599	0.331	0.055	0.560	0.385
	890	0.217	0.65	0.118	0.096	0.642	0.262	0.056	0 524	0.42	0.044	0.471	0.485
70:30	830	0.368	0.589	0.043	0.201	0.68	0.119	0.128	0.678	0,194	0.108	0.671	0.221
	850	0.302	0.636	0.062	0.152	0.687	0.161	0.094	0.645	0.261	0.080	0.677	0.303
	870	0.247	0 663	0.090	0.118	0.672	0.21	0.072	0.589	0.339	0.060	0.550	0,39
	890	0.20	0.671	0.129	0.096	0.633	0.271	0.058	0.514	0.428	0.047	0.464	0.489
60:40	830	0.329	0.618	0.053	0.184	0.686	0.13	0.122	0.673	0.205	0.105	0.663	0.232
	850	0.27	0.657	0.073	0.141	0.688	0.171	0.092	0.636	0.272	0.080	0.605	0.315
	870	0.22	0.679	0.101	0.113	0.667	0.22	0.071	0.579	0.350	0.061	0.539	0.40
	890	0.18	0.679	0.141	0.092	0.627	0.281	0.058	0.503	0.439	0.048	0.455	0.497

4. Cracking of $n\text{-}C_4H_8$. The equilibrium extents to which the primary reactions involved in the cracking of $n\text{-}C_4H_8$ take place can be calculated from the equations:

$$x_{4b} = \frac{(K_{p_{4b}})^{0.5}}{1+(K_{p_{4b}})^{0.5}}; \quad x_{4c} = \left(\frac{K_{p_{4c}}}{K_{p_{4c}}+4}\right)^{0.5};$$

$$x_{4d} = \frac{(K_{p_{4d}})^{0.5}}{1+(K_{p_{4d}})^{0.5}}; \quad x_{4e} = \frac{\sqrt[3]{K_{p_{4e}}}}{1+\sqrt[3]{K_{p_{4e}}}},$$

while that for reaction (4) can be found graphically. Calculations[6] from thermodynamic data[29] showed that in the range 520–630°C reactions (4), (4b), and (4e) are almost completely displaced to the right; the degree of transformation according to reaction (4d) varies from 94.7% to 92.3% and the degree of transformation according to reaction (4c) varies from 46.6% to 80.8%.

5. Transformation of C_4H_6. The temperature dependence of the equilibrium constant for the dimerisation of C_4H_6 is given by the equation[5]:

$$R\ln K_{p_{5a}} = \frac{-34\,825}{T} + 5.968 + 11.0755\log T + 10^{-4}T - 1.288\times10^{-6}T^2.$$

The equilibrium degrees of dimerisation, calculated[6] from the equation

$$x_{5a} = \left[1 - \frac{1}{(1+4K_{p_{5a}})^{0.5}}\right],$$

are given in the following table

T, °K	800	820	840	860	880	900
x_{5a}	0.891	0.861	0.818	0.767	0.707	0.633

The cracking reactions (5b) and (5c) at 500–600°C are almost completely displaced to the right.

6. Isomerisation reactions. Equations for calculating the equilibrium constants for the isomerisation reactions in the gaseous phase are summarised in Table 4.

All these equations show satisfactory agreement with calculations using the latest thermodynamic data.

TABLE 4. Equations for the temperature dependence of the equilibrium constants of the isomerisations (in the gaseous phase).

Reaction	Equation	Temp. range, °C	Ref.
$n\text{-}C_4H_{10} \rightleftarrows Me_2C{=}CH_2$	$\log K_{p_{4a}} = \frac{358+93}{T} - 0.802+0.055$	—	33
	$\log K_{p_{4a}} = \frac{2318}{4.575T} - 0.929$	150	37
$n\text{-}C_4H_8 \rightleftarrows Me_2C{=}CH_2$	$\log K_{p_{4b}} = \frac{304}{T} - 0.528\pm0.020$	265—426	38
$EtCH{=}CH_2 \rightleftarrows MeCH{=}CHMe$	$\log K_p = \frac{619.3}{T} - 0.335$	200—380	39
$EtCH{=}CH_2 \rightleftarrows$ *cis*-$MeCH{=}CHMe$	$\log K_p = \frac{387}{T} - 0.393$	200—380	39
$EtCH{=}CH_2 \rightleftarrows$ *trans*-$MeCH{=}CHMe$	$\log K_p = \frac{606}{T} - 0.524$	200—380	39

With increase in temperature the equilibrium is displaced towards the formation of $n\text{-}C_4H_8$; the equilibrium composition of the $n\text{-}C_4H_8$ mixture changes little with temperature[40]:

T, °K	800	820	840	860	880	900
$EtCH{=}CH_2$	0.303	0.312	0.32	0.328	0.336	0.344
cis-$MeCH{=}CHMe$	0.297	0.294	0.292	0.289	0.288	0.285
trans-$MeCH{=}CHMe$	0.40	0.394	0.388	0.383	0.376	0.371

7. Reactions of water vapour. The equilibrium constants for reactions (7a) to (7d) can be calculated using the following simplified equations[17]:

$$\log K_{p_{7a}} = \frac{-6830}{T} + 1.75\log T + 2.5, \quad (7a)$$

$$\log K_{p_{7b}} = \frac{-4300}{T} + 1.75\log T + 0.8, \quad (7b)$$

$$\log K_{p_{7c}} = \frac{-2150}{T} + 2.3, \quad (7c)$$

$$\log K_{p_{7d}} = \frac{-8919}{T} + 9.01. \quad (7d)$$

The equilibrium extents to which all these reactions take place increase with temperature and, for example, amount to 50–60%[33] at 600°C and stoichiometric ratio of the reacting substances; under the conditions of the dehydrogenation of butene, however, because of the large excess of water vapour (and also hydrogen) relative to the quantity of "carbon" on the catalyst, the equilibria for reactions (7a), (7b), (7c), (7e), and (7f) are almost completely displaced to the right.

It is impossible to examine the equilibria for the oxidation or reduction of the metal oxides usually present in dehydrogenating catalysts, since usually the form of compound in which the oxides are actually present in the catalyst and the reactions involved in the conversion of the metal from one valency state to another are still unknown.

4. CATALYSTS

There have been many attempts to use different combinations of oxides as catalysts for the dehydrogenation of alkanes, particularly butane, but only the aluminium–chromium oxide catalysts promoted with potassium oxide have found industrial application[2]. The optimal concentration of Cr_2O_3 in catalysts for the dehydrogenation of $n\text{-}C_4H_{10}$ to $n\text{-}C_4H_8$ is apparently close to 10%.[2] Many properties of these catalysts (the optimal concentration of chromium oxide, the influence of promoting additives, methods of preparation, the porous structure of the Al_2O_3 and the catalysts, the influence of the catalyst particle size, the degree of dispersion of the chromium oxide, and the relationship between the catalytic activity and the electrical conductivity) have been described in detail[3]. A characteristic property of aluminium–chromium catalysts is their sensitivity to the poisoning effect of water; thus in the dehydrogenation of isobutane the activity of the catalyst begins to decrease at a concentration of water vapour in the original gas greater than 1 mg litre^{-1}, but the activity also decreases with decrease in the moisture content of the isobutane (below 1 mg litre^{-1}).[41] This feature (the decrease in activity in the total absence of water) has unfortunately not yet been explained. An extremely important feature of aluminium–chromium catalysts is the change in their activity during dehydrogenation; the yield of butene[19] increases sharply in the first few minutes after regeneration, reaches a maximum (see

Fig. 1§), and then decreases¶. The reduced activity in the first minutes is attributed[16] to poisoning of the catalyst by the water formed by the reaction of the excess (relative to Cr_2O_3) of oxygen with the hydrocarbons. The activity of the catalyst increases as this excess of oxygen is used up and the water (and also CO_2) is desorbed. The decrease in the activity of the catalyst after the maximum is usually attributed to an increase in the deposition of carbon, although this is unlikely to be the only cause.

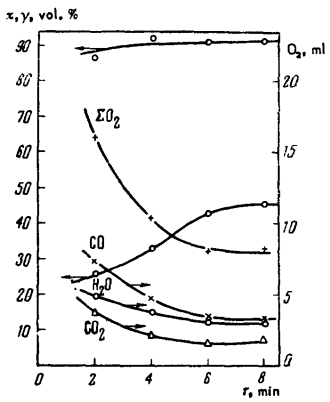


Fig. 1. Change in the yield of n-C_4H_8, selectivity, and quantity of combined oxygen during dehydrogenation of butane for 8 min at 570° and a space velocity of 1000 h^{-1}:
x — yield of n-C_4H_8; γ — selectivity;
O_2 — quantity of oxygen in H_2O, CO_2, and CO;
ΣO_2 — total quantity of O_2; τ — duration of dehydrogenation.

Many papers have been devoted to the study of the influence of the oxidation and reduction of aluminium–chromium[18,22,24,25,43] and also chromium[44–46] catalysts on their activity in dehydrogenations (of butane or cyclohexane). In most of this work it has been shown unambiguously that after reduction (with sufficient desorption of water) the activity of the catalysts increases†; if, however, the desorption of the water formed during the reduction is inadequate, the activity of the catalyst may even decrease as a result.

The compositions of the industrial catalysts for the dehydrogenation of butene are more varied than those of the catalysts for the dehydrogenation of butane; the compositions and properties of these catalysts are given in Table 5.

At present, the chief catalyst used in Canada and Britain is Dow-B, and the chief catalysts used in the USA are Shell-205, Dow-B, and Phillips-1490.[47] The chief advantages of the Shell catalysts are: prolonged operation without regeneration, low dilution with water vapour, durability, and mechanical strength; a disadvantage of the catalysts is their low selectivity[48]. High yields and selectivity are the chief advantages of the catalyst Dow-B,[49] although this catalyst also has many disadvantages (sensitivity to poisoning by most oxides and metals, higher yields of carbonyl compounds and alkynes, and shorter operational life[48]).

Method of dehydrogenation may be mentioned briefly. Three methods for dehydrogenating butane to butene are known[50–55]: in tubular periodic-action reactors with external heating and immobile catalyst, in assemblies with moving catalyst spheres, and in assemblies with a fluidised bed of fine catalyst particles.

In all countries the dehydrogenation of butene on the industrial scale is carried out in reactors without external heating on an immobile catalyst[1]. The single-stage dehydrogenation of butane to buta-1,3-diene is carried out[1] at reduced pressure in a system of reactors, each of which

§ An earlier paper[19] gave data on the change in the yields only at 505°; analogous data have been obtained at 570° and 590°.

¶ The same relationships were observed in the dehydrogenation of isopentane[42,114].

† An increase in the activity of the aluminium–chromium catalyst as a result of its reduction by hydrogen was also observed[42] in the dehydrogenation of pentane and isopentane.

TABLE 5. Composition and properties of some industrial catalysts for the dehydrogenation of butene*.

Catalyst (firm's designation)	Composition, %	Conditions of use (in industrial reactors)	Characteristics		References
			yield of C_4H_8, mole %	selectivity, mole %	
No. 1707	72.4MgO + 4.6CuO + 18.4Fe_2O_3 + 4.6K_2O	630°, space velocity (with respect to C_4H_8) 400 h^{-1}, dilution to molar ratio $C_4H_8:H_2O$ = 1 : 10, duration of dehydrogenation 1 h, duration of regeneration 1 h	20.2	73	1, 47
Shell-105	90Fe_2O_3 + 4Cr_2O_3 + 6K_2CO_3	620°, space velocity 400 h^{-1}, dilution to molar ratio 1 : 10, duration of dehydrogenation without regeneration about one week	19–20.3	69–72	1, 2, 47, 48
Shell-205	same as Shell-105, but with higher K_2CO_3 content	621–677°, space velocity 500 h^{-1}, dilution to molar ratio 1 : 8, dehydrogenation for 24 h, regeneration for 1 h	19.5–20.5	73–75	1, 2, 47
Phillips-1490	unknown	649°, dilution to molar ratio 1 : 10, operation for one year without regeneration	20.5	76	47
Dow-B	$Ca_3Ni(PO_4)_2$ stabilised with 2% Cr_2O_3 on carrier	593–677°, space velocity 125–175 h^{-1} dilution to molar ratio 1 : 20, dehydrogenation for 15–30 min, regeneration for 15–50 min	42.5–49.5	90–94**	49, 94

* See also Ref. 94.

** Maximal yield and selectivity.

is periodically switched over to dehydrogenation, regeneration, and preliminary operations (blow-through, evacuation, etc.). In the dehydrogenation the temperature of the catalyst (mixed with inert packing) is reduced by 15–20 deg and this supplies the heat required for the process. The operational conditions are chosen in such a way that the heat of dehydrogenation is equal to the heat of regeneration[47,56]. Many sources point out the need to purge the catalyst with hydrogen after regeneration[57].

5. REACTION RATES

The study of the rates of the reactions taking place in the dehydrogenation of n-C_4H_{10} and n-C_4H_8 involves many difficulties associated with the complexity (large number of reactions) and non-steady nature (change in activity during a single cycle) of the process.

An outstanding contribution to the study of the mechanism and kinetics of the catalytic dehydrogenation of organic compounds has been made by the work of Balandin and his school. On the basis of the principles of the multiplet theory of catalysis, he developed the mechanism of dehydrogenations[58,59], proposed a general equation for the rate of dehydrogenation of organic compounds[60,61], made a detailed study of the rate of dehydrogenation of n-C_4H_8 on chromium and mixed oxide catalysts[62–65], obtained general relationships[66] for the dehydrogenation of n-C_4H_{10}, and studied the dehydrogenation[67–69] of n-C_4H_{10} + n-C_4H_8 mixtures. Important studies of the kinetics of the dehydrogenation of n-C_4H_{10} and n-C_4H_8 have been carried out by Kagan, Lyubarskii, Pshezhetskii, and their coworkers[3]. Let us now examine the equations for the rates of individual reactions.

Rate of Dehydrogenation

The reaction n-$C_4H_{10} \rightleftharpoons$ n-$C_4H_8 + H_2$. The equations at present known for the rate of dehydrogenation of n-butane to butene are given in Table 6.

TABLE 6. Equations for the rate of dehydrogenation of n-C_4H_{10} to n-C_4H_8 over aluminium–chromium catalysts.

No.	Rate equations	Temperature range, deg	Apparent activation energy E_1, kcal mole^{-1}	Refs.
1	$\frac{dx_1}{d\tau} = k_d \exp\left(h - \frac{1}{RT}\right) E_1 \cdot \frac{P_1}{\Sigma z_r \cdot P_r}$	—	—	59,60
2	$-\frac{dP_1}{d\tau} = \frac{k_1 P_1}{1 + k_1/k_2 P_1 + k_3/k_4 P_2}$	260–500	—	70
3	$-\frac{dC_1}{d\tau} = k_1 \frac{C_1}{C_2^{0.5}} - k_{hydr} C_2^{0.5} \cdot C_3$	460–500	40.0±1.0	71,72
4	$\ln \frac{D}{D-M} = a\tau^b$	500–550	—	73
5	$\frac{dx_1}{d(W/F)} = \frac{k_1 (P_1 - P_2 P_3/Kp)}{(1 + k_1' P_1 + k_2' P_2 + k_3' P_3)^3}$	570 480–550	36.0 43.9	4 53
6	$\frac{dx_1}{d(W/F)} = k_1 \frac{P_1}{P_2^{0.5}} \left(1 - \frac{P_2 P_3}{K_p P_1}\right)$	510–550	41.4±2.2	83,115

Note. According to data[116] obtained in a flow-circulation assembly, the rate of dehydrogenation of n-C_4H_{10} on a reduced aluminium–chromium–potassium catalyst at 525–570° is described by the equation

$$k_1 P_1 \left(1 - \frac{P_2 P_3}{K_p P_1}\right), \quad E = 46 \pm 3 \text{ kcal mole}^{-1}.$$

In these equations, the left-hand side gives expressions for the rate of dehydrogenation; P_1, P_2, P_3, and P_4 are the partial pressures of n-C_4H_{10}, n-C_4H_8, H_2, and C_4H_6 respectively; C_1, C_2, C_3, and C_4 the concentrations of the reagents (in the same order as in the case of P_i); $k_d = \frac{k_0 \alpha}{h - 1/RT}$, in which k_0 is a constant, and h and α the coefficients in the function for the distribution of the active centres of the catalyst with respect to activation energies $\Phi(E) = \alpha \exp(hE)$; z_r the relative adsorption coefficients for the reacting substances, and P_r their partial pressures; k_1, k_2, and k_3 — in Eqn. (2) — the rate constants for the elementary reactions (formation and decomposition of the surface radical) or, in Eqn. 5 (with primes) the constants of the adsorption equilibrium for n-C_4H_{10}, n-C_4H_8, and H_2; k_1 — in Eqns. (3), (5), and (6) — the rate constant; W the weight of catalyst; F the rate of supply of butane; x_1 and M the degrees of dehydrogenation; D the maximum degree of dehydrogenation attainable on a given catalyst at a given temperature; τ the duration of contact, and a and b coefficients.

Equation 1 was proposed by Balandin, who claims[61] that it expresses the rate of dehydrogenation of hydrocarbons, alcohols, and amines over metallic and oxide catalysts at pressures which are not too low and at a distance from equilibrium. This equation is readily transformed into Frost's equation[75] for monomolecular irreversible reactions. Let us demonstrate this. For a given catalyst, the quantity $k_d \exp(h - 1/RT).E = \varphi(T) = K$. Replacing the partial pressures by the degree of dehydrogenation x_1 and integrating from 0 to x_1, we obtain

$$k\tau = \int_0^{x_1} \frac{\frac{1-x_1}{1+x_1} z_1 + \frac{x_1}{1+x_1} z_2 + \frac{x_1}{1+x_1} z_3}{\frac{1-x_1}{1+x_1}} dx = \int_0^{x_1} \left[z_1 + (z_2 + z_3) \frac{x_1}{1-x_1} \right] dx_1 = (z_2 + z_3) \int_0^{x_1} \left(\frac{z_1}{z_2 + z_3} + \frac{x_1}{1-x_1} \right) dx_1,$$

from which

$$\frac{K}{z_2 + z_3} \tau = \frac{z_1}{z_2 + z_3} x_1 - \ln(1 - x_1) - x_1 = \ln \frac{1}{1-x_1} - \left(1 - \frac{z_1}{z_2 + z_3}\right) x_1.$$

Introducing the symbols

$$\frac{K}{z_2 + z_3} = k_1 \text{ and } 1 - \frac{z_1}{z_2 + z_3} = \beta,$$

we obtain

$$k_1 \tau = \ln \frac{1}{1-x_1} - \beta x_1.$$

An analogous transformation[106] in more general form was given earlier[59,61].

Equation 2 (Pshezhetskii, Lyubarskii, and coworkers) is analogous in form to the first equation of Balandin, but the coefficients of the equations (for the partial pressures of the reagents) are interpreted in different ways. According to Pshezhetskii, Lyubarskii, and coworkers[70], these coefficients give the ratio of the rate constants of the elementary stages of the reaction; according to Balandin[60,61], these coefficients are the relative constants of the adsorption equilibrium for the reagents, as confirmed by the much higher value of the constants for the adsorption equilibrium compared with the value of the dehydrogenation rate constant[76].

The equation of Pshezhetskii and Lyubarskii is also readily transformed into Frost's equation. Integration of this equation gives[70]:

$$\left(\frac{k_1}{k_2}-\frac{k_3}{k_4}\right)P_1^0\alpha-\left(1+\frac{k_3}{k_4}\right)P_1^0\ln(1-\alpha)=\frac{k\omega}{V},$$

where P_1^0 is the initial partial pressure of C_4H_{10}, $\alpha = \frac{P_1^0 - P_1}{P_1}$ the degree of transformation; V the rate of flow of gas, and ω the free volume of the catalyst. Dividing both sides of the equation by $\left(1+\frac{k_3}{k_4}P_1^0\right)$ and introducing the symbols

$$\frac{\left(\frac{k_1}{k_2}-\frac{k_3}{k_4}\right)P_1^0}{1+\frac{k_1}{k_2}P_1^0}=-\beta \text{ and } \frac{k_1}{1+\frac{k_3}{k_4}P_1^0}=K,$$

we obtain

$$K\frac{\omega}{V}=\ln\frac{1}{1-\alpha}-\beta\alpha.$$

The value of β here is in fact negative, since[70] $\frac{k_3}{k_4} \gg \frac{k_1}{k_2}$ (for example[70], at 500°, $k_1/k_2 = 3.8$ and $k_3/k_4 = 100$).

Equations 1 and 2 are applicable only for low degrees of dehydrogenation, since they make no allowance for the back reaction.

Equation 3 (Lyubarskii and Pshezhetskii) is an empirical equation; it makes allowance for the reverse reaction of hydrogenation[72] and is more conveniently written in the form (retaining the symbols used in the original[72]):

$$w=k_1\frac{C_1}{C_2^{0.5}}\left(1-\frac{C_2C_3}{K_CC_1}\right),$$

since $k_1/k_{hydr} = K_C$ is the equilibrium constant. In this form the equation is applicable up to equilibrium.

Equation 4 (Obolentsev and coworkers[73]) is of characteristic form‡ and is also distinguished by the fact that as $\tau \to 0$ the reaction rate also tends to 0; the existence of an induction period for this example is difficult to explain although for the thermal dehydrogenation of ethane the form of the kinetic curve apparently indicates the existence of an induction period[78].

Equation 5 was derived, on the basis of a general method[79], from the Langmuir isotherm. In the derivation it was assumed[4] that the dehydrogenation involves two active centres; the equation makes allowance for the back reaction.

Equation 6[6,74,115] is analogous to the Lyubarskii–Pshezhetskii equation. Some of the data for its derivation are given in Figs. 2 and 3§. The experiments were carried out in a flow assembly with an immobile catalyst layer (particle size 0.7 mm) at maximal activity. In the range 510–550°C, the apparent activation energy is 41.4 ± ± 2.2 kcal mole^{-1}, and in the range 550–570°C E = 15.7 ± ± 0.7 kcal mole^{-1}.[83,115] The observed decrease in the value of E here is due to retardation by internal diffusion.

The establishment of the kinetic relationships for dehydrogenation in a fluidised catalyst bed is extremely important. From the general relationship[80] it follows that

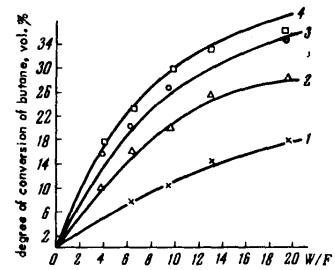


Fig. 2. Dependence of the degree of conversion of n-C_4H_{10} on the rate of supply and temperature (°C): 1) 510°; 2) 530°; 3) 550°; 4) 570° (atmospheric pressure).

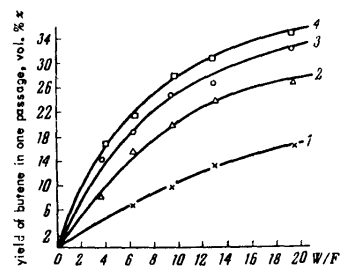


Fig. 3. Dependence of the yield of n-C_4H_8 on the rate of supply of butane and temperature (for numbering see Fig. 2).

the degree of dehydrogenation in a reactor containing a fluidised bed is less than that in a reactor containing an immobile layer, and that this difference increases with increase in the linear velocity and decrease in the particle size of the catalyst in the fluidised bed; this is due to the fact that some of the gas slips through the fluidised bed in the form of bubbles[74]. The rate of dehydrogenation in this reactor¶ is given by an equation of the same type, with the introduction of a coefficient φ which makes allowance for the change in the reaction rate as a result of the fact that some gas slips through[74]:

$$\frac{dx_1}{d(w/F)}=\varphi k_1\frac{P_1}{P_2^{0.5}}\left(1-\frac{P_2P_3}{K_pP_1}\right),$$

in which

$$\varphi=\left[1-\left(\frac{w-w_{cr}}{w}\right)^2\right]^{0.5},$$

where w is the linear velocity of the gas in the reactor and w_{cr} the rate of the start of formation of the fluidised bed; other conditions being equal, w_{cr} depends on the particle size[6].

The reaction n-$C_4H_8 \rightleftharpoons C_4H_6 + H_2$. The published kinetic equations for this reaction are given in Table 7; the symbols are the same as those used earlier. It can be seen that some of the equations in Table 7 are

‡ An equation of this type was justified by Kazeev[77].

§ The experimental data are given in detail elsewhere[6].

¶ The results of the dehydrogenation of n-C_4H_{10} in a fluidised bed in small experimental assemblies have been described by Aliev et al.[95]

TABLE 7. Equations for the rate of the reaction $n\text{-}C_4H_8 \rightleftharpoons C_4H_6 + H_2$ over various oxide catalysts.

No.	Equations	Catalyst	Conditions	E_a, kcal mole^{-1}	Refs.
1	$\frac{dx_2}{d\tau} = \frac{k_2 C_2}{C_2 + z_3 C_3 + z_4 C_4}$	chromium, chromium oxide	pressure 180–350 mmHg, 535–559°C 550–600°C	34.34–34.14 26.26–27.93	63
2	$\frac{d(H_2)}{d\tau} = \frac{104.5\,[C_4H_8]}{[C_4H_8] + 9.5\,[C_4H_6] + 0.82\,[H_2]}$	ditto	dilution to molar ratio $n\text{-}C_4H_8 : H_2O = 1:10$, 560°C	19.1	64
3	$-\frac{dP_2}{d\tau} = \frac{k_2 P_2}{1 + k_2/k_3 P_2}$	aluminium–chromium	dilution with nitrogen, $P_2 = 0.1$–0.3 atm, 450–500°C	27±1	70
4	$-\frac{dC_2}{d\tau} = k_2 C_2^{0.2}$	ditto	ditto	27±1	81
5	$\frac{dx_2}{d(W/F)} = \frac{k_2 (P_2 - P_3 P_4 / K_p)}{(1 + k_2' P_2 + k_3' P_3 + k_4' P_4)^2}$	No. 1707	dilution with water vapour, 640–668°C	17.6	5
6	$-\frac{dC_2}{d\tau} = k_2 C_2^3$	not indicated	dilution with water vapour, 570–630°C	not calculated	82
7	$\frac{dx_2}{d(W/F)} = k_2 P_2^{0.35}\left(1 - \frac{P_3 P_4}{K_p P_2}\right)$	industrial oxide	dilution with water vapour, 580–620°C	24.8	6,16

similar in form to the equations for the rate of dehydrogenation of $n\text{-}C_4H_{10}$; only equations 5 and 7 make allowance for the reverse hydrogenation reaction.

Equations 1 and 2 (Balandin, Bogdanov, and coworkers[63,64]) are identical; the numerical coefficients are given for 560° and P_{total} = 180–350 mmHg. The difference between equation 3 (Pshezhetskii and coworkers[70]) and Balandin's equation is in a term making allowance for retardation by the reaction products. Shcheglova and Pshezhetskii[81] did not detect this retardation, apparently because of differences in the experimental procedures: in the study of the retarding influence of C_4H_6 its concentration in the original mixture[81] did not exceed the quantity formed by dehydrogenation of pure $n\text{-}C_4H_8$; in the work by Balandin and coworkers[63,64], the quantity of C_4H_6 added was 3–10 times greater than the quantity of C_4H_6 formed. It should be emphasised that in these experiments of Balandin and coworkers[63], as in the dehydrogenation of butane[62], a decrease in the value of E with increase in temperature was observed.

Equation 5 is completely analogous to the corresponding equation for the rate of dehydrogenation of butane, so that all that was previously said regarding this equation is applicable to the equation for the rate of dehydrogenation of $n\text{-}C_4H_8$.

Equation 6[82] was derived from experimental data obtained on a large-scale assembly in a tubular reactor with 8 litres of catalyst. It appears that some methodological factors associated with this are responsible for the unusual order of the reaction.

Equation 7 is applicable for a catalyst with maximal activity[6,16]. In fact, the activity of the industrial catalyst for which this equation was obtained does not remain constant throughout the operational period; the time dependence of the rate constants for the dehydrogenation of $n\text{-}C_4H_8$, calculated[6] from published data[16], is shown in Fig. 4. The temperature dependence of the maximal values of k_2 is given by the equation[16]:

$$\log k_2 = \frac{-24\,800}{4.575T} + 5.03,$$

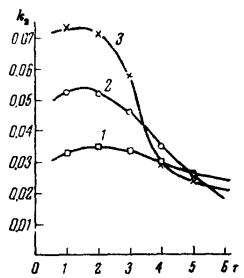


Fig. 4. Time dependence of the rate constants for the dehydrogenation of $n\text{-}C_4H_8$:
1) 580°; 2) 600°; 3) 620°; τ = duration of dehydrogenation, h.

and for any value of the time within the operational period from 1 h to 6 h the values are given by the equations[6] (for example, for 600°):

$$\text{from 1 h to 4 h, } k_\tau = k_2 \times 0.9924\tau^{0.062} \exp(-0.0109\tau^{2.5}),$$
$$\text{from 4 h to 6 h, } k_\tau = k_2 \times 5.97\tau^{-1.88}.$$

It is assumed[16] that the change in the activity of the dehydrogenation catalyst is due to a change in chemical composition under the influence of the reaction medium.

Dehydrogenation of butane–butene mixtures at reduced pressure. No mathematical description of the rate of dehydrogenation of $n\text{-}C_4H_{10}$ + + $n\text{-}C_4H_8$ mixtures at reduced pressure (that is, the rate of the single-stage dehydrogenation) has yet been published, but a number of papers have described fairly clearly the main regular features of this process.

On an aluminium–chromium catalyst, the rate of the reaction $n\text{-}C_4H_{10} \rightleftharpoons n\text{-}C_4H_8 + H_2$ is greater[67,70] than the rate of the reaction $n\text{-}C_4H_8 \rightleftharpoons C_4H_6 + H_2$. According to the data of Pshezhetskii et al.[70] the difference in the rates of these

reactions decreases with temperature and at 500°C $w_1 : w_2 = 2.7$; according to the data of Shcheglova and coworkers[67] the rate of the first reaction at 600°C is almost six times the rate of the second reaction. The establishment of the fact that the reactions involved in the formation of C_4H_6 from n-C_4H_{10} take place in succession is extremely important. It has been established[34] using ^{14}C that in the dehydrogenation of n-C_4H_{10} + n-C_4H_8 on an aluminium–chromium catalyst at 600°C and P_{total} = = 250 mmHg the rate of the reaction n-$C_4H_8 \rightarrow C_4H_6 + H_2$ is approximately twenty-five times the rate of the reaction n-$C_4H_{10} \rightarrow C_4H_6 + 2H_2$. From this work[34] it also follows that the rate of dehydrogenation of n-C_4H_{10} to n-C_4H_8 is smaller than the rate of dehydrogenation of n-C_4H_8 by a factor of about 2.5; the reasons for the discrepancy between these and other data[67,70] are not clear.

General relationships describing the influence of temperature, volume rate, pressure, and composition of the original n-C_4H_{10} + n-C_4H_8 mixture on the yield of butadiene and the selectivity of the process have been published[84,85]. They may be summarised as follows. Under the conditions studied[85] the yield of C_4H_6 increases with increase in temperature, increase in the concentration of n-C_4H_8 in the original mixture, and decrease in pressure. When the catalyst is purged for a short period with hydrogen after regeneration, the yield and selectivity increase appreciably (by 10–15%); the selectivity also increases with increase in the volume rate and with decrease in the temperature or pressure. An important characteristic of the process is the ratio of the quantities of n-C_4H_8 in the reaction products and in the original mixture. If this ratio is equal to unity, the butene is not used up and the process can be regarded as a single-stage process in the sense that only butane has to be added to the butane–butene mixture returned for recycling. This parameter, called the degree of single-stage character, increases with decrease in the concentration of butene in the original mixture, with decrease in the volume rate, with decrease in temperature, and with increase in pressure; purging of the catalyst with hydrogen also increases the degree of single-stage character (by 15–20%). Moreover, all the characteristics of the process also depend on the duration of the dehydrogenation[85]: the yield of butadiene at first increases, passes through a maximum, and then decreases†; the selectivity increases continuously and the degree of single-stage character decreases.

Reactions involved in the cracking of n-C_4H_{10} and n-C_4H_8. The catalytic and thermal cracking of hydrocarbons obeys a first-order equation. For n-butane the rate constant of the thermal decomposition (for a degree of transformation 7–9%, when secondary reactions can be neglected) is determined from the equation[86]:

$$\log k_c = \frac{-73\,900}{4.575T} + 17.05.$$

According to other data[87], for all straight-chain alkanes from C_3 to C_{10}, the activation energy of the primary thermal decomposition has an average value of 63 kcal mole^{-1}. According to more recent data[88], for n-C_4H_{10} E = = 58.7 kcal mole^{-1}; the same value was obtained in recently published work[89] in which the order of the reaction involved in the thermal decomposition of n-C_4H_{10} was found to be 3/2.

The rate of the cracking of butane in its catalytic dehydrogenation has been examined by a few authors[4,6,53]. It has been assumed[4] that the rates of the cracking of n-C_4H_{10} and n-C_4H_8 under dehydrogenation conditions are approximately equal; the cracking reaction is homogeneous and of first order. Since the kinetic data were obtained[4] for a single temperature (571°C) the equation obtained by Paul and Marek[86] is used for the cracking rate constant, although it is pointed out that the rate of cracking in the presence of an aluminium–chromium catalyst is slightly greater than the rate of thermal cracking (but by a factor of not more than 5–10). It is considered[5] that in the dehydrogenation of butene on catalyst No. 1707 the cracking of butane is also a first-order thermal reaction

$$\log k_c = \frac{-60\,000}{4.575T} + 15.2734,$$

the rates of the cracking of n-C_4H_{10} and n-C_4H_8 being approximately equal. The same assumption, made by Tyuryaev[6], is justified by the fact that on the highly selective catalyst used[6] only a comparatively small quantity of butane and butene decompose by cracking reactions (not more than 15% of the total butane reacting). With these assumptions, the rate of cracking is[83]:

$$\frac{dx_c}{d(W/F)} = k_c \frac{P_{C_4H_{10}} + P_{C_4H_8}}{P_{H_2}}.$$

For the dehydrogenation of butane on this catalyst[83,115]:

$$\log k_c = \frac{-40\,000 + 3600}{4.575T} + 7.0 \pm 1.0.$$

For dehydrogenation on another catalyst[53] the rate of cracking was given approximately by the equation

$$\frac{dx_c}{d(W/F)} = k_c(P_{C_4H_{10}} + P_{C_4H_8}), \text{ and } \log k_c = \frac{-38\,300}{4.575T} + 8.06.$$

Comparison of the cracking rate constants from this equation and from the equation for thermal cracking[87,88], shows that the rate of cracking increases slightly in the presence of the dehydrogenating catalyst.

There are very few papers on the thermal cracking of n-butene. The cracking of MeCH=CHMe has been studied in detail[8]. At 570–700°C and a degree of transformation in the range 5–12%, the rate of decomposition is described approximately by a first-order equation:

$$\log k_c = \frac{-53\,000 + 900}{4.575T} + 11.40.$$

The rate of the cracking of butene during its dehydrogenation on catalyst No. 1707 was mentioned above[5]; on another industrial catalyst[16] the cracking of n-C_4H_8 is negligibly small so that the study of this reaction is of no particular interest.

The decomposition of butadiene is an important reaction in the dehydrogenation of butene[5,6,63,90]. Work on the rate of thermal transformation of C_4H_6 has been reviewed[91]. The chief reaction involved in the thermal transformation of C_4H_6 at 400–700°C and atmospheric pressure[15] is polymerisation; the reaction is of second order with E = 28 kcal mole^{-1} and

$$\log k = \frac{-6400}{T} + 7.3 \pm 0.04.$$

† On the specimen studied[85], the yields of C_4H_6 were:

duration of dehydrogenation, min:	5	7	10	13
yield of C_4H_6 in one passage, mole %:	18	19	17	16

At reduced pressure[91,92], the chief reaction in the transformation of butadiene is dimerisation; the reaction is of second order[91] with

$$\log k = \frac{-26\,800}{4.575T} + 11.14.$$

In the dehydrogenation of n-C_4H_8 on catalyst No. 1707[5] (with dilution by water vapour) decomposition of the butadiene formed involves chiefly catalytic cracking (5b) and thermal dimerisation; the rate of the first reaction is

$$r = \frac{kP_{C_4H_6}}{(1 + k_{C_4H_6}P_{C_4H_6} + k_{H_2}P_{H_2} + k_AP_A)^2},$$

with

$$\log k = \frac{-5000}{4.575T} + 0.2385,$$

(the subscripts A denote aromatic compounds). The dimerisation is a second-order reaction with

$$\log k = \frac{-25\,000}{4.575T} + 8.0632.$$

The dimer may also undergo cracking[5] with the formation of H_2, CH_4, C_2H_4, C_2H_6, and toluene; this reaction is a thermal reaction of first order, with

$$\log k = \frac{-31\,000}{4.575T} + 6.0323.$$

In the dehydrogenation of n-C_4H_8 on an industrial catalyst the cracking of C_4H_6 according to Eqn. (5c) is described by an equation of the same type[90] as that given by Beckberger and Watson[5] (with the exception of the term k_AP_A), or by the simpler equation[6]:

$$\frac{dx}{d(W/F)} = \frac{kP_{C_4H_6}}{(1 + aP_{C_4H_6})^2}.$$

The constants in these equations naturally depend on the form of equation used[6,90]. The activity of the catalyst with respect to the cracking reaction decreases during the operational period[90]. The time dependence of the rate constant is shown in Fig. 5; the curves are described by the equation

$$k_\tau = k\exp(-0.429\tau^{0.613}),$$

where τ is the duration of the operational period and k the rate constant for τ = 1 h.

Rate of carbon formation. As can be seen from Section 2, the quantity of "carbon" deposited on the catalyst in the dehydrogenation of n-butene is determined by the rate of decomposition of C_4H_6, for example, according to reactions (5b) or (5c); carbon formation in the dehydrogenation of n-butane must be regarded as an independent process[26]. Only one paper[26] has been published on the kinetics of carbon deposition on an aluminium-chromium catalyst in the dehydrogenation of n-C_4H_{10}; other papers[50,96,97] merely record the fact that "carbon" is formed or give values for the extent of carbon deposition on the catalyst under specific dehydrogenation conditions. The quantity of "carbon" formed in the dehydrogenation of butane is independent of the particle size of the catalyst and the volume rate of supply of butane and is determined by the equation[26]: $C_C = A\tau^{0.684}$, where C_C is the quantity of "carbon" as a percentage of the weight of catalyst, and τ the duration of dehydrogenation or the time for which the catalyst is present in the reactor, min‡,

$$\log A = \frac{-6620}{T} + 6.57.$$

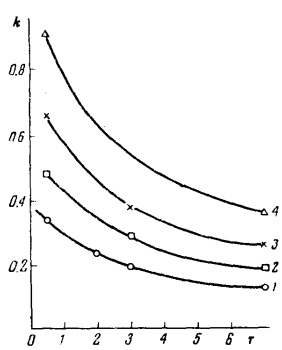
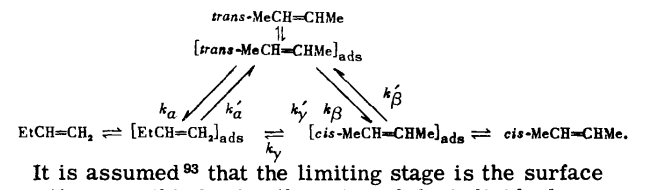


Fig. 5. Time dependence of the rate constants for the transformation of C_4H_6: 1) 560°; 2) 580°; 3) 600°; 4) 620°.

The kinetic equation obtained[26] is analogous in form to equations found earlier for the rate of carbon formation in the cracking of petroleum products on an aluminosilicate catalyst[98] or in the dehydrogenation of cyclohexane on an aluminium–molybdenum catalyst[99].

The isomerisation of n-C_4H_{10} and n-C_4H_8. Although isomerisation in the dehydrogenation of n-butane and n-butene has been reported many times[47,73], there are no quantitative data on the rates of the reactions n-C_4H_{10} ⇌ iso-C_4H_{10} and n-C_4H_8 ⇌ $Me_2C{=}CH$ in the presence of dehydrogenating catalysts. The rate of the isomerisation $EtCH{=}CH_2$ ⇌ *trans*-MeCH=CHMe ⇌ *cis*-MeCH=CHMe on an aluminium–chromium catalyst has been studied in detail[93]. The following reaction mechanism has been proposed:



It is assumed[93] that the limiting stage is the surface reaction; on this basis, the rates of the individual reactions are:

$$-\frac{dP_1}{d\tau} = \frac{dP_t}{d\tau} + \frac{dP_c}{d\tau} = \frac{k_\alpha K_1P_1}{1+K_1P_1} + \frac{k'_\gamma K_1P_1}{1+K_1P_1},$$

$$-\frac{dP_c}{d\tau} = \frac{dP_1}{d\tau} + \frac{dP_t}{d\tau} = \frac{k_\gamma K_cP_c}{1+K_cP_c} + \frac{k'_\beta K_cP_c}{1+K_cP_c},$$

$$-\frac{dP_t}{d\tau} = \frac{dP_c}{d\tau} + \frac{dP_1}{d\tau} = \frac{k_\beta K_tP_t}{1+K_tP_t} + \frac{k'_\alpha K_tP_t}{1+K_tP_t}.$$

In these equations, P represents the partial pressures and K the adsorption equilibrium constants; the subscripts 1, c, and t refer to $EtCH{=}CH_2$, *cis*-MeCH=CHMe, and *trans*-MeCH=CHMe, and k and k' are the rate constants for the forward and back reactions. The following values were found for the activation energies (kcal mole^{-1}):

for $EtCH{=}CH_2$ ⇌ *trans*-MeCH=CHMe, E = 7.9;

for $EtCH{=}CH_2$ ⇌ *cis*-MeCH=CHMe, E = 5.0;

and for *trans*-MeCH=CHMe ⇌ *cis*-MeCH=CHMe, E = 12.6.

‡ According to data[117] published after the present manuscript was submitted, $C_C = A + B\tau$.

In the dehydrogenation of n-butane, the isomeric composition of the mixture of n-butenes obtained[6,50] is close to the equilibrium composition. The part played by skeletal isomerisation of n-C_4H_{10} and n-C_4H_8 in the dehydrogenation is small[6].

The reaction of water vapour with "carbon". Reactions (7e) and (7f), observed in the dehydrogenation of n-C_4H_8 (with dilution by water vapour), is of zeroth order both with respect to H_2O and with respect to the concentration of carbonaceous deposits on the catalyst[5,6];

$$\log k = \frac{-39\,000}{4.575T} + 5.09375, \text{ according to Beckberger and Watson (Ref. 5),}$$

or

$$\log k = \frac{-41\,600}{4.575T} + 8.02475, \text{ according to Tyuryaev (Ref. 6).}$$

The zeroth order with respect to water is attributed[6] to the very large excess of water vapour, and the order with respect to "carbon" probably depends on the reaction mechanism. The rate constant decreases with time[6] (see Fig. 6).

Reaction involved in the regeneration of the catalysts. Despite the importance of this question, the rate and chemistry of the processes taking place in the regeneration of dehydrogenating catalysts have been insufficiently studied. Thermograms have been obtained[23,101] for the regeneration of chromium catalyst specimens on which carbon was deposited during the decomposition of alcohols and dehydrogenation of cyclohexane; combustion of the carbonaceous deposits began at 240°. It was established[23,102] that the carbonaceous deposits contain components richer in hydrogen ("tars") and components with low hydrogen content ("coke").

The rate of combustion of carbonaceous deposits in the regeneration of aluminium–chromium catalysts has been little studied[6,100,103]. In the kinetic range (300–350°)[103] the combustion is of second order with respect to "carbon" and of first order with respect to oxygen, that is, $-\frac{dc}{d\tau} = kc^2P_{O_2}$, and E = 31.1 kcal mole^{-1}. The rate constant depends on the composition of the carbonaceous deposits: the value of k decreases with decrease in the hydrogen content; on the other hand, the hydrogen content of the carbonaceous deposits decreases with increase in the deposition of carbon on the catalyst. The rate of regeneration of aluminosilicate cracking catalysts obeys the same equation[104]; the value of E here is similar (26.6 kcal × × mole^{-1}).

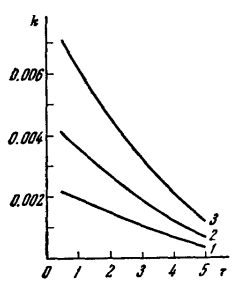


Fig. 6. Change in the rate constants for the reaction of water vapour with "carbon":
1) 560°; 2) 580°; 3) 600°.

In the regeneration of a catalyst for the dehydrogenation of butane in a fluidised bed[100] at 600–650°, the combustion takes place in the outer-diffusion range; the reaction rate is given by an equation of the same type

$$-\frac{dc}{d\tau} = k_d c^2 P_{O_2},$$

where k_d is the apparent rate constant, which depends on the rate of diffusion

$$\log k_d = \frac{-2800}{4.575T} + 0.14 \text{ or } k_d = 0.0482(T/273)^{1/2}.$$

The rate of oxidation of an aluminium–chromium catalyst during regeneration is given by an equation of the form $C = A\tau^n$ where C is the CrO_3 concentration, wt.%, A the temperature coefficient, and τ the duration of the regeneration, min.[6,100] For the catalyst specimen studied[6,100], the reaction takes place in the kinetic range up to 550°C, after which diffusion retardation is observed; in the kinetic range, n = 0.098 and $\log A = \frac{-815}{T} + 0.766$.[6] An interesting feature is that integration of the equation proposed[105] for the rate of reduction of MoO_3 to MoO_2 during treatment of an aluminium–molybdenum catalyst with hydrogen, $\frac{1}{W_0}\frac{dW}{d\tau} = -a\tau^{-b}$, gives an equation of the same form with approximately the same exponents§.

The relationship between the activity and the concentration of sexivalent chromium after regeneration has been studied by a number of workers[18,22,24,25].

Rate of desorption of water. The change in the water content with time during regeneration of the catalyst for the dehydrogenation of n-butane is described satisfactorily by the equation[6,100]: $q/q_0 = A_1\tau^{0.61}$, where q_0 is the initial or equilibrium concentration of H_2O on the catalyst and q the concentration of H_2O, wt.%, at time τ, min.

The desorption rate constant also depends on the initial water content[6,100]:

for q_0 = 0.2–0.4 mg g^{-1}

$$\log A_1 = -\left(\frac{800}{T} + .49\right);¶$$

for q_0 = 0.1–0.2 mg g^{-1}

$$\log A_1 = \frac{-1680}{T} + 0.65;$$

for $q_0 < 0.1$ mg g^{-1}

$$\log A_1 = \frac{-3400}{T} + 2.61.$$

This relationship is attributed[6] to the fact that part of the water is adsorbed physically on the catalyst and part is

§ $\frac{dW}{W_0} = -a\tau^{-b}d\tau\frac{W}{W_0} = \frac{a}{1-b}\tau^{1-b}$. According to John and co-workers[105], b = 0.904, that is, $1 - b$ = 0.096 (compare with n = = 0.098).

¶ Misprint in Russian text (Ed. of Translation).

chemisorbed; on heating, the physically adsorbed water is desorbed first (with a smaller thermal effect). The magnitude of the apparent activation energy for the removal of chemisorbed water should be close to the activation energy of chemical reactions. This is confirmed by the results obtained[6]; from the last equation it follows that E = = 15.6 kcal mole^{-1}. With increase in the extent of the heat treatment of the catalyst, its activity for the dehydrogenation of butane increases[100].

There are no published data on the kinetics of carbon decomposition, combustion of carbonaceous deposits, and oxidation of catalysts for the dehydrogenation of butene.

6. NEW DEHYDROGENATION REACTIONS

The dehydrogenations examined up to the present are reversible; the yields of butene or buta-1,3-diene usually do not exceed 80% of the equilibrium degrees of dehydrogenation. This means that in the two-stage dehydrogenation the yields (of n-C_4H_8 in the first stage and of C_4H_6 in the second stage) cannot exceed about 45% and that the yield of C_4H_6 in the single-stage dehydrogenation of butane in a vacuum can at best reach 20%. Thus the scope of ordinary dehydrogenation methods is clearly limited.

Recent years have seen the discovery of other dehydrogenation reactions in which the hydrogen is bound in the form of water, for example[107]:

$$n\text{-}C_4H_8 + \tfrac{1}{2}O_2 \rightarrow C_4H_6 + H_2O.$$

These reactions, which may be called oxidative dehydrogenation reactions, are displaced almost completely to the right. On the basis of published data[107-113], these dehydrogenation reactions can be divided into three groups.

1. Dehydrogenation of alkenes on oxide catalysts in the presence of oxygen[107,108]. The reaction is carried out at 450–540° at a volume rate of supply of n-C_4H_8 equal to 200–600 h^{-1} with dilution by water vapour. In a reactor with an immobile layer of catalyst[107] (a mixture of oxides of metals from Groups V and VI of the Periodic System) the yield of C_4H_6 reaches 50% and the selectivity is about 90%. The chief side-reaction is extensive oxidation of the hydrocarbons (to CO_2 and CO); almost no hydrogen is present. In a reactor with a fluidised catalyst bed the yield of C_4H_6 could be increased[108] to 70% without loss of selectivity. It is reported[109] that catalysts based on bismuth tungstate, bismuth molybdate, and bismuth phosphate are active for the oxidative dehydrogenation of butene.

2. Dehydrogenation of alkanes to alkadienes in the presence of iodine[110,111,113]. The process is described by the following equations[110]

$$n\text{-}C_4H_{10} + 2I_2 \rightleftharpoons C_4H_6 + 4HI,$$
$$2HI + MO \rightarrow H_2O + MI_2,$$
$$MI_2 + \tfrac{1}{2}O_2 \rightarrow MO + I_2.$$

MnO_2 has been used as metal oxide[111]. The reaction is carried out at 520–550° at a molar ratio $C_4H_{10}:I_2$ = 1 : 1.43 in the presence of metal oxides which readily absorb the HI formed. The use of the oxides achieves two results: displacement of the dehydrogenation equilibrium to the right and regeneration of iodine. The quantity of iodine required[110] can be decreased by adding oxygen to the reaction mixture to bring about "internal regeneration" of iodine:

$$2HI + \tfrac{1}{2}O_2 \rightarrow I_2 + H_2O.$$

A C_4H_6 yield of 52% has been achieved[110] with a selectivity of 75%.

3. Dehydrogenation of alkanes on solid catalysts in the presence of oxygen. A number of patents[112] show that it is possible to carry out the reaction

$$n\text{-}C_4H_{10} + O_2 \rightarrow C_4H_6 + 2H_2O.$$

The catalysts consist of a mixture of metal oxides (for example, 97.5 Fe_3O_4 + 2.5 LiOH) or a mixture of metal halides (for example, 2.08 KBr + 1.09 r.e.e. chlorides + + 0.82 AgBr on α-Al_2O_3). In the first the original mixture (in moles): n-C_4H_{10} + 15H_2O + 0.85O_2 + 0.07I_2 + + 0.115Cl_2 is passed over a catalyst at 575°C and a liquid C_4H_{10} volume rate of 0.5 h^{-1}. Under these conditions the yield of C_4H_6 is 54% and the selectivity 66%.

Passage of a mixture with C_4H_{10} : air : I_2 : H_2O = 1 : 4.76 : : 0.04 : 2.9 (in moles) at 500°C over a catalyst of the second type gives a C_4H_6 yield of 48.7% and selectivity 79.1%.

Oxidative dehydrogenation reactions open up new possibilities for the preparation of alkadienes; the study of these reactions is of considerable scientific interest.

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THE ABSOLUTE RATE CONSTANTS OF THE ELEMENTARY STAGES OF RADICAL POLYMERISATION

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The elementary stages in a polymerisation radical chain reaction can in most cases be summarised as follows:

$$M \rightarrow M^{\cdot}, \quad (1)$$

$$M^{\cdot} + M \xrightarrow{k_p} MM^{\cdot}, \quad (2)$$

$$2M^{\cdot} \xrightarrow{k_t} P. \quad (3)$$

Reaction (1) is initiation, that is, formation of radicals from inactive molecules of the monomer M, reaction (2) is propagation of the reaction chain, leading to growth of the polymeric radical, and reaction (3) leads to the formation of the final reaction product — inactive polymer — and termination of the reaction chain.

Kinetic study of the polymerisation scheme (1) shows that for long reaction chains the dependence of the steady-stage reaction rate V_{st} on the elementary constants is given by the equation

$$V_{st} = I^{1/2} \frac{k_p}{k_t^{1/2}} [M]. \quad (4)$$

Thus the quantity $k_p/k_t^{1/2}$ can be determined from the reaction rate if the rate of initiation I is known. Methods for measuring rates of initiation have been described in detail[1]. $k_p/k_t^{1/2}$ can also be determined[2] from the dependence of the length of the polymer chain on the rate of polymerisation, given by the equation

$$\frac{1}{P_n} = \frac{k_M}{k_p} + \frac{k_t}{k_p^2} \frac{V_{st}}{[M]^2}, \quad (5)$$

where P_n is the number-average degree of polymerisation, usually determined from the viscosity of the polymer solutions, and k_M is the rate constant for chain transfer via the monomer. Schulz and coworkers[3] proposed equations which can be used to calculate the value of $k_p/k_t^{1/2}$ directly from the viscosity-average degree of polymerisation P_η. The value of $k_p/k_t^{1/2}$ can also be found by measuring the intensity of light scattering in the reaction vessel during the polymerisation[4].

The individual absolute values of the constants k_p and k_t cannot, however, be determined on the basis of Eqns. (4) or (5) alone. An additional equation relating these quantities depends on kinetic measurements of the lifetime of the radicals under non-steady reaction rate conditions.

There are several methods for making non-steady kinetic measurements. In the case of photochemical initiation, the absolute values of the elementary reaction rate constants can be found by intermittent illumination using a rotating sector. An interesting modification of this method has been proposed[5] for studying reactions in a flow system, initiated by γ-radiation; the glass tube used as reaction vessel was wound in a spiral round a ^{60}Co source placed in a lead cylinder with a longitudinal opening. The extensive use of the intermittent-illumination method for studying chain reactions began about 1945.

The theory of the method has been described in detail[1,6]. The practical details are as follows: measurements are made of the steady-state rates with continuous illumination V_{st} and with the rotating sector V_{int} with light–dark interval T chosen in such a way that V_{int}/V_{st} lies in the range 0.50–0.708. The graph giving the theoretical dependence of V_{int}/V_{st} on T/τ is then used to find T/τ and hence the lifetime of the free radicals τ. This is related to the constants k_p and k_t by the equation

$$\frac{k_p}{k_t} = \frac{\tau V_{st}}{[M]}. \qquad (6)$$

The method of intermittent illumination does not require a specially sensitive procedure and is simple in operation, but its accuracy is low compared with other methods.

A modified rotating-sector method combined with dilatometric recording of the steady-state rate has been used[7]. These measurements are made at low degrees of conversion, and in the authors' opinion they give better agreement between the theoretical curves and the experimental points than the ordinary rotating-sector method.

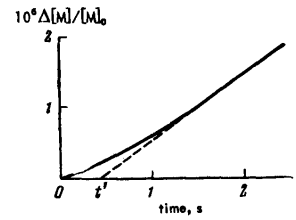
The method of initial non-steady kinetics is based on the determination of the lifetime of the radicals during the establishment of the steady state. The modern form of the theory of this method was put forward by Burnett[8]. The Figure gives the experimental curve for the kinetics of styrene polymerisation and shows clearly the initial non-steady section. The intercept cut off on the time axis by producing the subsequent steady-state section is $t' = \tau \ln 2$. If τ is known, k_p/k_t can be calculated from Eqn. (6).

These equations refer to quadratic chain termination. It follows from Eqn. (4) that the steady-state rate of polymerisation here is proportional to the square-root of the rate of initiation or, for photochemical initiation, the square root of the incident light intensity. Thus the applicability of Eqn. (4) is verified experimentally from the dependence of the reaction rate on the intensity of illumination. Deviations from the degree of the dependence $n = 0.5$ show that the bimolecular chain termination is accompanied by monomolecular chain termination (with respect to the radical heading the chain), for example, on an impurity X

$$P + X \rightarrow \text{products}. \qquad (7)$$

In the range $n = 0.5$–0.6, the corrections to the values of k_p and k_t, determined on the assumption that n is equal to exactly 0.50, do not exceed 20%,[9] that is they lie within the limits of the usual accuracy of the determination of kinetic constants. Methods have been proposed for determining these corrections.

Various methods have been proposed for recording the kinetic curve in the initial non-steady stage; these are in



Initial non-steady kinetics for the polymerisation of styrene[11].

fact based on measurement of the increase in temperature in the reaction vessel as a result of the exothermic reaction in the time interval in which it is possible to neglect the loss of heat from the reaction vessel to the thermostat liquid, that is, under so-called pseudo-adiabatic conditions. In the first experiments[10,11], the change in the dielectric constant of the reaction mixture and the change in the refractive index of the liquid were recorded[12]. The increase in temperature was also recorded directly by means of a thermocouple[13] or thermistors[14]. Bengough[15] developed a dilatometric method for recording non-steady kinetics. A method for determining the value of k_p/k_t from light scattering measurements was recently proposed[16].

Study of the initial non-steady kinetics has the indisputable advantage that with the short time interval for a single measurement it is possible to carry out a large number (up to 20) separate measurements on the same specimen, with an appreciable increase in accuracy. The accuracy of the determination of τ does not exceed 0.1 s, however, and this restricts the applicability of this method, particularly to reactions where the lifetime of the radicals is less than 0.5–0.7 s.

Another group of methods for measuring non-steady kinetics involves the study of reactions after photochemical initiation is stopped. These do not differ in principle from the methods described above, but they exhibit certain characteristic methodological features. In most of them, the rate of the spontaneous thermal reaction is taken into account. To record the reaction rate, Bamford and Dewar[17,18] proposed a viscosimetric method based on the determination of the number-average degree of polymerisation by measurement of the viscosity of the resulting polymer during and after photochemical initiation. Details of the method have been given in a review[19] and a monograph[1]. A modification of the method, which makes it possible to determine the constants directly from the viscosity-average degree of polymerisation and also makes allowance for monomolecular termination, was recently proposed by Okamura and coworkers[20]. The viscosimetric method is rather tedious, involves the solution of cumbersome equations, and has a low accuracy. A method has also been described for determining the chain-growth constant by measuring the rate of emulsion polymerisation under certain conditions[21].

The photochemical after-effect[22] has also been used in the dilatometric determination of polymerisation constants. Benson and North[23] examined some experimental complications associated with the dilatometric measurements (loss of heat from the dilatometer, heating of the reaction mixture as a result of illumination, absence of thermal initiation, presence of monomolecular chain termination, etc.).

We developed a method[24] for determining the value of k_p/k_t from the non-steady kinetics of the photochemical after-effect by measuring the increase in temperature in the period of pseudo-adiabatic conditions. When a slow background reaction, which may be a thermal reaction or a reaction brought about specially by means of constant weak illumination, is taking place in a system, it is found that when the illumination (main initiation) is switched off after a steady-state rate has been attained, the quantity of substance ΔM_{qu} which has reacted when the reaction is quenched is given by the equation

$$\Delta M_{qu} = k_p n_0 [M](t-\theta) + \frac{k_p}{k_t}[M]\ln\left(\frac{1-q^{-2k_t n_0(t-\theta)}}{1-q}\right), \quad (8)$$

where n_0 is the steady-state concentration of radicals resulting from the background reaction, θ the moment at which the illumination is switched off, and $q = (V_{st} - V_0)/(V_{st} + V_0)$, where V_{st} and V_0 are the steady-state rates of the photoinitiation and the background reaction.

If the reaction vessel in which the background reaction takes place is brought into thermal equilibrium with a thermostat, the increase in temperature for the subsequent switching-on and switching-off of the illumination (main initiation) will be determined by the second term on the right-hand side of Eqn. (8). The total quantity of substance converted at the quenching of the photoinitiated reaction is obtained for $t \to \infty$:

$$\Delta\Delta M = -\frac{k_p}{k_t}[M]\ln\frac{2V_0}{V_{st}+V_0}. \quad (9)$$

This equation can be used to find k_p/k_t.

It can be seen that in the photochemical after-affect method, unlike the initial non-steady kinetics method, we record not the duration of the non-steady state, but the quantity of substance converted, which is proportional to the increase in temperature. This quantity is usually determined with a higher accuracy than the duration of the non-steady state. Independent determination of V_0 and V_{st} by the dilatometric method also increases the accuracy of the determination of k_p/k_t.

The method also makes it possible to carry out measurements where no purely thermal reaction takes place in the system.

An expression identical to (9) was obtained by Bateman and Gee[25] for the quantity of oxygen absorbed at quenching of the photoinitiated oxidation.

Most of the methods for determining the rate constants of the elementary stages of radical polymerisation involve the use of complex highly sensitive instruments, which represent the limits of measuring techniques at the present stage of their development. Methods involving the simpler dilatometric measurements give less reliable results. Almost all methods involve the accurate recording of the start or finish of the photochemical reaction. This feature imposes an additional restriction on the range of materials for which the constants can be measured. This difficulty can apparently be avoided by using a recently-proposed method[26] in which a solution of rapidly-decomposing initiator is sprayed into the monomer, with efficient mixing.

Data on the determination of rate constants for radical polymerisation up to 1958 were collected and critically reviewed by Bagdasar'yan[1]. The present paper will examine chiefly work published in the last five years (up to March 1964), including earlier data for the sake of completeness where necessary.

Sometimes only the overall rate of polymerisation was determined, and information even on the magnitude of $k_p/k_t^{1/2}$ can be obtained from these data only by additional calculation; if the thermal initiator, its concentration, and, most important, the rate of decomposition and efficiency of initiation, determined by an independent method, are known, it is possible to calculate the rate of initiation and the value of $k_p/k_t^{1/2}$. The kinetic behaviour of a number of monomers on polymerisation does not correspond to the kinetic scheme of reactions (1)–(3), and if a new reliable scheme is not proposed, calculation of the constants for these monomers is impossible. Data for individual monomers are given below.

Styrene. Analysis of the most reliable data leads[1] to the following values for the constants† for styrene polymerisation

$$k_p/k_t^{1/2} = 380\exp(-6500/RT), \quad (10)$$

$$k_p = 9.35\times10^6\exp(-7250/RT), \quad (11)$$

$$k_t = 7.1\times10^8\exp(-1500/RT). \quad (12)$$

The values of $k_p/k_t^{1/2}$ recently obtained from the length of the polymer chains[20,27-29] are almost the same as those calculated from Eqn. (10). Henrici-Olivé and Olivé[29], on the basis of their measurements and published data, obtained the expression

$$k_p/k_t^{1/2} = 135\exp(-5700/RT), \quad (13)$$

which is almost the same as (10). Moreover, in these experiments attention was directed to the part played in chain termination by the primary radicals formed by decomposition of the initiator. It was shown[20,27] that at low concentrations of the usual initiators (azoisobutyronitrile, benzoyl peroxide) relative to the monomer, the recombination of the primary radicals with polymeric radicals can be neglected, but with an initiator such as phenylazotriphenylmethane, which gives stable triphenylmethyl radicals with low activity, it is necessary to make allowance for termination by primary radicals even at an initiator concentration of 10^{-4} M.[28] An important part is also played by primary radicals in chain termination for initiation of styrene polymerisation by the thermal decomposition of the polymeric peroxides of dibasic organic acids[30].

The value of k_p at 40°, determined by Burnett and Lehrle[31] by the emulsion polymerisation method is only 14% lower than the value calculated from Eqn. (11).

Methyl methacrylate. On the basis of a thorough critical analysis of a large amount of experimental data, Bagdasar'yan[1] obtained the following equations for the constants for methyl methacrylate polymerisation

$$k_p/k_t^{1/2} = 95\exp(-4500/RT), \quad (14)$$

$$k_p/k_t = 1.35\times10^{-2}\exp(-4300/RT). \quad (15)$$

Recent years have seen the appearance of a fairly large number of papers devoted to the kinetics of the polymerisation of methyl methacrylate; studies have been made not only of the initial stage of polymerisation, but also of the kinetics at high degrees of conversion and in solvents with

† The values for all the constants are given in mole litre^{-1} s^{-1}.

different viscosities. These data will be discussed later. The results of the determination of the kinetic constants at very low degrees of conversion are compared in Table 1 with the values obtained from Eqns. (14) and (15).

Schulz and coworkers[3] found that in the polymerisation of methyl methacrylate in benzene solution at 30–80° the equation

$$k_p/k_t^{1/2} = 53\exp(-4200/RT), \quad (16)$$

is satisfied.

It can be seen from the above data that the results of recent work show good agreement with Eqns. (14) and (15); the deviation from these equations is determined by the accuracy of the measurements. Values of $k_p/k_t^{1/2}$ were determined[27,34] viscosimetrically from the relationship between molecular weight and characteristic viscosity for non-fractionated polymers, and this method has been supplemented[3] by initiation by means of an initiator labelled with ^{14}C and by determination of the molecular weight of individual fractions by an osmotic method. The rate of initiation has been determined using ^{14}C [33] and from the rate of the reaction of radicals from the initiator azocyclohexane-1,1′-carbonitrile with diphenylpicrylhydrazyl in chloroform solution[32]. The ratio $k_p/k_t^{1/2}$ was determined from the initial non-steady kinetics using a thermocouple[32,33] and dilatometrically from the photochemical after-effect[34,35].

The ratio of the rate constants for chain termination by disproportionation k_{dis} and by recombination of the radicals k_{rec} was also determined[3]

$$\log(k_{dis}/k_{rec}) = 2.89 - 1000/T, \quad (17)$$

which gives for the difference in the energies of activation $E_{dis} - E_{rec} = 4.6$ kcal mole^{-1}. From Eqn. (17) at 60°, $k_{dis}/k_{rec} = 0.78$, which, although it differs from the accepted[1] value of 0.67, produces a change of only 4–5% in the calculated value of $k_p/k_t^{1/2}$. Determination of k_{dis}/k_{rec} from the quantity of radioactive initiator fragments in the polymer gave the value 1.35 at 60°.[36]

North and coworkers[37] studied the polymerisation of methyl methacrylate in the range from -60° to -20° in ethyl acetate solution. The reaction was initiated by ethylsilver, whose rate of decomposition was used to calculate the rate of initiation. The kinetics of the polymerisation are described by the equation;

$$V = 1.7\exp(-5100/RT)\,[\mathrm{MMA}]^{3/2}\,[\mathrm{AgC_2H_5}]^{1/2}.$$

Extrapolation of Eqn. (17) shows that at these low temperatures, termination takes place chiefly by the recombination of radicals. The values of $k_p/k_t^{1/2}$ determined with this assumption from the length of the polymer chains are greater by a factor of 2.5 than the value expected from Eqn. (14). It is suggested that ethylsilver forms a complex with methyl methacrylate. The reaction is initiated by the reverse decomposition of this complex to metallic silver and a free radical.

Atkinson and Cotten[22] studied the polymerisation of methyl methacrylate in aqueous solution at 25° and obtained the values $k_p = 75$ litre mole^{-1} s^{-1} — Eqns. (14) and (15) give $k_p = 252$ — and $k_t = 1.8 \times 10^4$. Although k_p does not differ greatly from the usual value, the rate of termination in water is greater by three orders of magnitude than that in organic systems.

Ethyl methacrylate. In the range 35–100°, for polymerisation "in bulk" with azoisobutyronitrile initiator, the viscosimetric method gave the value[38] $k_p/k_t^{1/2} = 77.6\exp(-4220/RT)$. The degree of polymerisation was determined from the characteristic-viscosity relationship for fractionated polymers.

n-Propyl methacrylate. The rotating sector method at 30°[39] gave $k_p/k_t = 0.070$, $k_p = 467$, and $k_t = 4.5 \times 10^7$. The rate of initiation was determined from the diphenylpicrylhydrazyl consumption.

n-Butyl methacrylate. $k_p/k_t^{1/2} = 0.116$ at 30°[39] and 0.196 at 60°.[40] The last value was determined without allowance for k_{dis}/k_{rec}, but differs from the value calculated from the rate of decomposition of the initiator by only 15–30%. From these two points, $k_p/k_t^{1/2} = 50\exp(-3500/RT)$. At 30° "in bulk" $k_p/k_t = 3.62 \times 10^{-5}$ [39] and in ethyl acetate solution $k_p/k_t = 9.1 \times 10^{-5}$.[35] Making use of the value of $k_p/k_t^{1/2}$, we have $k_p = 147$–362 and $k_t = (1.0$–$1.6) \times 10^7$.

Isobutyl methacrylate. Khanna and coworkers[38] obtained the value $k_p/k_t^{1/2} = 55.3\exp(-4000/RT)$. The value obtained at 60°[40] is $k_p/k_t^{1/2} = 0.180$, which is only 14% less than that found by Khanna and coworkers[38] by the same method. In ethyl acetate solution at 30°, $k_p/k_t = 9.1 \times 10^{-5}$,[35] which with the above data gives $k_p = 109$ and $k_t = 1.2 \times 10^7$ at 30°.

t-Butyl methacrylate. Grant and Grassie[41] found for the polymerisation "in bulk" and in benzene solution at 20–90° the value $k_p/k_t^{1/2} = 0.0955$ at 25° and $E_p - \frac{1}{2}E_t = 3.85$ kcal mole^{-1}. The value of $k_p/k_t^{1/2}$ was determined viscosimetrically from the length of the polymer chains; it was assumed that $k_{rec} = 0$. The rotating-sector method gave $k_p/k_t = 6.5 \times 10^{-3}\exp(-3300/RT)$, so that $E_p = 4.4$ kcal mole^{-1} and $E_t = 1.1$ kcal mole^{-1}; at 30°, $k_p = 410$ and $k_t = 1.4 \times 10^7$.

Comparison of the data for the butyl methacrylates shows that the rotating-sector method gives a value for k_p which is 2–4 times that given by the dilatometric method of Benson and North[34]. It is difficult to give preference to either set of data, particularly since the determination of $k_p/k_t^{1/2}$ and k_p/k_t by the rotating-sector

TABLE 1. Values of k_p and k_t for methyl methacrylate.

Temperature, °C	$k_p/k_t^{1/2}$		$10^4 k_p/k_t$	
	from Eqn. (14)	measured	from Eqn. (15)	measured
22.5	0.049	0.058[33]	0.93	0.87 [33]
30	0.056		1.12	4.0 [34]
30				1.4* [34]
30				1.43*[35]
32	0.052	0.044[32]	1.18	1.9 [32]
40	0.072	0.096*[34]	1.41	2.3* [34]
60	0.11	0.128[37]		
60		0.144**[37]		
70	0.135	0.13**[37]		
70		0.15*[37]		

* In ethyl acetate solution.

** In toluene solution.

method was carried out "in bulk" and the determination of k_p/k_t by the dilatometric method was carried out in the less viscous ethyl acetate solution.

Nonyl methacrylate. The value $k_p/k_t^{1/2} = 24.3 \exp(-2590/RT)$ has been obtained[38] (the structure of the nonyl group is not indicated). The value $k_p/k_t = 1.8 \times 10^{-4}$ was obtained for 3,5,5-trimethylhexyl methacrylate in ethyl acetate solution at 30°.[35] If we assume that the same substance was studied in the two instances and neglect the difference in viscosity, calculation gives $k_p = 620$ and $k_t = 3.45 \times 10^6$ for 30°. The value of k_p is evidently several times too high.

Cetyl methacrylate. The viscosimetric method (by analogy with other methacrylates it was assumed that $k_{rec} = 0$) in the range 50–80° gave the expression[42] $k_p/k_t^{1/2} = 42.3 \exp(-2500/RT)$, which on extrapolation to 30° gives $k_p/k_t^{1/2} = 0.69$. Dobó and Friese[43] by rough calculation obtained $k_t = 3 \times 10^6$ at 24°, from which $k_p = 98$ at 30°.

A detailed study has been made, for the polymerisation of alkyl methacrylates, of the influence of viscosity on the magnitude of the polymerisation rate constants, noted by Bengough and Melville[44] in a study of the polymerisation of vinyl acetate at high degrees of conversion. North and coworkers[34,35] studied this effect by carrying out the polymerisation at a low degree of conversion in solvents with different viscosities, and found that for methyl methacrylate the value of k_t/k_p is inversely proportional to the viscosity throughout the entire range of viscosity studied $\eta = 0.42$–1000 cP, the lower value being less than the viscosity of the monomer. The value of k_t/k_p is proportional to $\eta^{-0.8}$ for butyl methacrylate and to $\eta^{-0.735}$ for nonyl methacrylate. Subsequently, like a number of other authors and following published conclusions[32,33,39], we shall assume that the chain-growth constant for alkyl methacrylates is independent of the viscosity and the length of the side chain (thus in the analysis it is sometimes more convenient to use the reciprocal k_t/k_p instead of the usual ratio k_p/k_t). The dependence of the termination rate constant on the length of the side-chain or the solvent, however, is evidently determined by the change in the rate of diffusion of the polymeric radicals and not by polar or steric effects, as has been suggested[27,38].

Since the values of k_t/k_p were given[34,35] for a low viscosity and the values of $k_p/k_t^{1/2}$ were determined "in bulk"[38], the individual rate constants calculated above from these data give merely an indication of the order of magnitude and have no claim to accuracy. It would be of interest to compare the constants obtained at the same viscosity. For this it is necessary to know the viscosity of each monomer, but we have been unable to find this information, apart from data[42] for the viscosity of methyl methacrylate (0.34 cP) and cetyl methacrylate (3.18 cP) at 70°. Calculation based on some rather arbitrary assumptions[45] gives values (Table 2) which reveal certain trends. It is evident that discussion of the influence of structure on the rate of termination for a system where it is determined by diffusion for some substances and lies in the kinetic range for other substances can lead to incorrect conclusions. As far as the values of the constants are concerned, Table 2 shows that at constant viscosity the decrease in the termination rate constant with increase in the dimensions of the ester group is irregular: with increase in the number of carbon atoms from 1 to 4 the termination rate constant decreases by a factor of 4–5,

TABLE 2. Dependence of the rate constants for the polymerisation of alkyl methacrylates on viscosity at 30° (approximate calculation).

Methacrylate	Viscosity of monomer, cP (estimated)	k_p		$10^{-7}k_t$	
		for η = 0.42 cP	"in bulk"	for η = 0.42 cP	"in bulk"
Methyl	0.42	270	270	2.5	2.5
n-Propyl	0.96	220	—	2.1	—
n-Butyl	1.23	62	93	0.68	0.065
Isobutyl	1.23	51	—	0.56	—
Nonyl	2.58	170	130	0.010	0.014

whereas further increase up to 9 leads to an increase in the constant by a further factor of 50–60. For a group of medium size (butyl) change in viscosity has a significant influence on the rate of termination, whereas for the bulky nonyl group the viscosity of the surrounding medium is no longer important.

Atherton and North[46] showed that for the copolymerisation of methyl methacrylate and vinyl acetate at 30° and 60° the termination is also determined by diffusion of the polymeric radicals.

According to North[34,35] diffusion termination takes place in three stages. The first stage involves the translational diffusion of two macroradicals into a position in which some segments of each chain are brought into contact. In the second stage, rearrangement or segmental diffusion takes place so that the ends of the two radicals approach sufficiently closely to one another for the third stage — chemical interaction — to take place. This scheme can be represented as follows:

$$P_A^{\cdot} + P_B^{\cdot} \rightarrow [P_A^{\cdot} \ldots P_B^{\cdot}], \quad (18)$$

$$[P_A^{\cdot} \ldots P_B^{\cdot}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [P_A : P_B], \quad (19)$$

$$[P_A : P_B] \xrightarrow{k_2} \text{products}. \quad (20)$$

It was shown[34] that the first stage is not the limiting stage. A model was proposed for the polymeric radical[35], in which the end of the chain is regarded as a cylinder whose axis coincides with the main C–C axis of the polymer chain and whose radius is determined by the dimensions of the lateral groups. From the dependence of the reaction rate on the size of the alkyl groups it was shown that the model corresponds to the experimental data. On the basis of scheme (18)–(20), Guertin[47] derived equations relating the rate of the individual stages to the rate and degree of polymerisation and also to the rate of initiation I, and obtained by calculation from the experimental data for methyl methacrylate[46] the values $k_{-1}/k_2\eta = 0.16$ P and $I\eta/k_1 = 9.16 \times 10^{-18}$ mole^2 P^{-1}.

Examination of these "hyper-elementary" stages became possible only as a result of the development of kinetic experiment and demonstrates how the fine effects of a chemical reaction can be revealed by modern methods.

Glycidyl methacrylate $CH_2-CHCH_2O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$.

The length of the polymer chains was determined[48] for polymerisation "in bulk" in the range 40–80°; the value of $k_p/k_t^{1/2}$ was also calculated from the rate of decomposition of the initiators. It was found that $k_{dis}/k_{rec} = 2.7$ and $k_p/k_t^{1/2} = 52.6 \exp(-3800/RT)$, which for 30° gives $k_p/k_t^{1/2} = 0.095$. The same authors[48], on the basis of the assumption that k_p/k_t is proportional to $k_p/k_t^{1/2}$ and

that E_t = 400 kcal mole^{-1}, obtained for glycidyl methacrylate, by comparison with the value of k_p/k_t for methyl methacrylate, the values $k_p = 4.13 \times 10^5 \exp(-4000/RT)$ and $k_t = 6.17 \times 10^7 \exp(-400/RT)$. From the data of Arbuzova and Efremova[49] for polymerisation "in bulk" at 70° with benzoyl peroxide initiator, it follows that the rate of polymerisation is approximately proportional to the square root of the initiator concentration. Assuming that the rate constant for the decomposition of benzoyl peroxide is 9.60×10^{-6} s^{-1} and that the efficiency of initiation is 0.8,[1] we obtain by calculation $k_p/k_t^{1/2} = 0.242$.

Benzyl methacrylate. Calculation by the same method from Majer's data[50] gives $k_p/k_t^{1/2} = 0.0338$ at 60° and 0.0362 at 70°.

Methyl acrylate. Data from recent papers, published simultaneously, which give the constant determined by the rotating-sector[51] and dilatometric[52] methods, differ little: $k_p = 1.45 \times 10^6 \exp(-4700/RT)$[51] and k_t = $= 3.55 \times 10^8$ [51] and 6.5×10^6.[52] In one[51] it was assumed that $k_{rec} \simeq 0$, and in the other[52] the rate of initiation was determined from the rate of consumption of diphenylpicrylhydrazyl. The determinations using diphenylpicrylhydrazyl apparently gave slightly high values for $k_p/k_t^{1/2}$.[41]

Butyl acrylate. Melville and coworkers[13,53], from initial non-steady kinetics using a thermocouple, recently obtained the value $k_p/k_t = 6.2 \times 10^{-5}$ at 25°. Benson and North[34], using the dilatometric method at 30°, obtained $k_p/k_t = 12.5 \times 10^{-4}$ "in bulk" (this result coincides with the earliest determination for butyl acrylate[53]) and 8.33×10^{-4} in ethyl acetate solution. Having determined the rate of initiation in separate experiments from the rate of consumption of diphenylpicrylhydrazyl, Bengough and Melville[53] obtained $k_p = 2100$ and $k_t = 3.3 \times$ $\times 10^8$ at 25°. These figures are greater, by factors of 4 and 400 respectively, than those adopted[1] on the basis of the values of $k_p/k_t^{1/2}$ found by other methods. For the activation energy it was found by $E_p - \frac{1}{2}E_t = 3.8$ kcal $\times$ $\times$ mole^{-1}. It is difficult to give preference to any of the data for butyl acrylate.

Methyl α-cyanoacrylate. For radical polymerisation with azoisobutyronitrile at 60°, $k_p/k_t^{1/2}$ = = 0.145 [55]; 100% efficiency of initiation was assumed in the calculations.

Vinyl chloride. Supplementary to earlier[1] contradictory results, Bengough and coworkers[7] obtained $k_p/k_t = 7.1 \times 10^{-7}$ at 25°, which is smaller by a factor of 10 than the value found by Burnett and Wright[56] by the rotating-sector method.

Vinyl acetate. Recent results[15,57-59] show good agreement with the equations adopted earlier[1]: $k_p = 1.13 \times$ $\times 10^6 \exp(-4200/RT)$ and $k_t = 3.12 \times 10^7$. The rate of polymerisation of vinyl acetate changes in a complex fashion with increase in the degree of conversion[44,60] and increases with increase in the viscosity of the solvent[46]. It was established[60] that in polymerisation "in bulk" the rate of diffusion of the macroradicals begins to exert a significant influence on the value of k_t from a degree of conversion equal to 2%, whereas k_p remains unchanged up to 50% conversion.

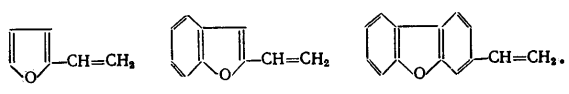
Vinyl benzoate. For polymerisation "in bulk", $k_p/k_t^{1/2} = 0.0255$ at 60° [61] and 0.14 at 79.6°.[62] The first figure[61] is more reliable, since the molecular weights were determined by an osmometric method and the length of the polymer chain was determined using an initiator labelled with ^{14}C. In the second case[62] the molecular weight was determined from the viscosity of solutions of the polymers from the formula for fractionated polymers, without appropriate corrections.

1-Vinylnaphthalene. The value $k_p/k_t^{1/2}$ = $= 3.92 \times 10^2 \exp(6150/RT)$ was obtained[63] from the dependence of the rate of polymerisation "in bulk" at 50–70° on the concentration of azoisobutyronitrile, with allowance for its rate of decomposition. The constant for chain transfer via the monomer is very high, $k_M = 0.03$. Naphthalene, which generally speaking reacts more readily with radicals than benzene, is activated further by the vinyl group.

Isopropenyl methyl ketone $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$.

For polymerisation "in bulk" and in toluene solution with benzoyl peroxide at 80°, from the length of the polymer chains, $k_p/k_t^{1/2} = 0.0278$.[64]

2-Vinylfuran, 2-vinylbenzylfuran, and 2-vinyldibenzylfuran



Calculation from the graphs given by Andreeva and Koton[65] on the assumption that Eqn. (4) applies (the dependence of the rate on the concentration of monomer and benzoyl peroxide initiator has not been determined experimentally) gives for polymerisation "in bulk" and in solution at 80–100° the values $k_p/k_t^{1/2} = 0.001$–0.0025 for 2-vinylfuran, 0.004–0.008 for 2-vinylbenzylfuran, and 0.006–0.021 for 2-vinyldibenzylfuran.

2-Vinylpyridine. For the rate of polymerisation with azoisobutyronitrile at 50–90°, the equation $V = 1 \times$ $\times 10^9 \exp(-2400/RT)$ s^{-1} has been obtained[66]. Calculation of the rate of initiation with the usual assumptions gives $k_p/k_t^{1/2} = 0.088$ at 50° and 0.281 at 90°, and $E_p - \frac{1}{2}E_t$ = = 5.2 kal mole^{-1}; extrapolation to 25° gives $k_p/k_t^{1/2}$ = = 7.4×10^{-3}. This calculation gives a value which differs from those for other vinylpyridines at 25° by a factor of only 3–4.

4-Vinylpyridine. Using the viscosimetric method at 25°, Onyon[67] obtained the values $k_p = 12$, $k_t = 3 \times 10^6$, and $k_M = 8 \times 10^{-3}$. The value $k_p/k_t = 1.9 \times 10^{-5}$ was obtained for polymerisation "in bulk" and in ethanol solution from the adiabatic increase in temperature[68]. The difference between these data and Onyon's data (0.4×10^{-5}) is apparently due to the low accuracy of the viscosimetric method for determining the values of k_p and k_t.

2-Methyl-5-vinylpyridine. The polymerisation was carried out[69] in benzene solution at 60–80° with azoisobutyronitrile and benzoyl peroxide. The rate is proportional to the square root of the initiator concentration. Calculation from the graphs gives values of $k_p/k_t^{1/2}$ which differ slightly for each initiator: 0.031 and 0.042 at 80° and 0.020 and 0.034 at 60°; extrapolation to 25° gives the

values 0.008 and 0.021. At 25°,[68] $k_p = 47$, $k_t = 3.5 \times 10^6$, and $k_M = 3.9 \times 10^{-3}$. In the determination of $k_p/k_t^{1/2}$ and k_M, the length of the polymer chains was calculated from the viscosity using a formula recalculated for the non-fractionated polymer with allowance for termination by chain transfer.

N-Vinylurethane[70]. The degree of polymerisation at 60° with azoisobutyronitrile was determined by an osmometric method. If it is assumed that $k_{rec} = 0$, the efficiency of initiation is $f = 0.59$ and $k_p/k_t^{1/2} = 0.52$ (if it is assumed that $k_{rec} > 0$, the value of f increases; for this initiator, however, f very rarely exceeds 0.6).

Acrylonitrile. The early data[1] are extremely contradictory. The value of k_p at 60° varies in the range 425–1960, and $k_t = 1.2 \times 10^7 - 7.8 \times 10^8$. For a long time it was assumed[71] that termination takes place by disproportionation of the polymeric radicals, but Bailey and Jenkins[72] showed, using tracer methods, that the chains are terminated by recombination of the radicals. Bengough[7] obtained the value $k_p/k_t = 3.4 \times 10^{-6}$ by a combined method in dimethylformamide solution at 25°, and the values $k_p = 52$ and $k_t = 5.0 \times 10^6$ by the thermocouple method "in bulk"[73] at a degree of conversion less than 0.1%, when the polymer has not yet precipitated from its solution in the monomer. These data show satisfactory agreement with our results[68] for dimethylformamide solution: $k_p = 2.35 \times 10^5 \exp(-6400/RT)$, $k_t = 1.8 \times 10^6$, and $E_t \simeq 0$.

The polymerisation of acrylonitrile in dimethylformamide was also studied by the rotating-sector method with initiation by γ-rays[74]. The reaction rate depends on the intensity of irradiation to the power 0.60. The Arrhenius relationship is observed in the range 0–60°; the values found were $E_p = 3.88$ kcal mole^{-1} and $E_t = 3.70$ kcal mole^{-1}. The results for 60°, $k_p = 660$ and $k_t = 8.65 \times 10^7$, agree with earlier data, within the limits of experimental error.

Comparison of the rates of the elementary stages of the polymerisation of nitrogen-containing monomers and styrene at 25° (Table 3) shows that the influence of the free electron pair of the nitrogen is the same for direct conjugation with the C=C double bond in acrylonitrile and for the transfer of this influence through the system of conjugated aromatic bonds in the vinylpyridines. The difference of one order of magnitude in the rates of chain termination indicate a sharp difference in the properties of the polystyrene radical compared with the polyacrylonitrile and polyvinylpyridine radicals. It is possible that the greater mobility of the polystyrene radical brings about more rapid segmental diffusion, compared with the relatively rigid polyacrylonitrile and polyvinylpyridine radicals.

Methacrylamide. For photopolymerisation in aqueous solution, initiated by H_2O_2, at 10–40°, the rotating-sector method[75] gave $k_p = 4 \times 10^5 \exp(-3700/RT)$ and $k_t = 1.3 \times 10^{10} \exp(-4000/RT)$. In the calculation of the rate of initiation, the quantum yield was taken as 0.87, by analogy with the reaction for acrylamide.

Esters of vinylphosphonic acid $CH_2=CH-PO(OR)_2$ were polymerised[76] at 50° with 2 mole % benzoic acid. The kinetic curves were used to calculate the values of $k_p/k_t^{1/2}$ for different esters: methyl 0.23, ethyl 0.14, n-propyl 0.23, isopropyl 0.12, n-butyl 0.36, isobutyl 0.22, and isopentyl 0.34.

TABLE 3.

	Acrylonitrile	4-Vinylpyridine	2-Methyl-5-vinylpyridine	Styrene
k_p	51		47	44
k_t	$1.8 \cdot 10^8$		$3.5 \cdot 10^8$	$4.0 \cdot 10^7$
$\frac{k_p}{k_t}$	$2.8 \cdot 10^{-5}$	$1.9 \cdot 10^{-5}$	$1.3 \cdot 10^{-5}$	$1.1 \cdot 10^{-6}$

Ethylene. The kinetics of the radical polymerisation of ethylene under the influence of suitable initiators under pressure in the liquid phase or in solution have been studied only recently. For polymerisation "in bulk" at a pressure of 40 atm under the influence of the photochemical decomposition of dimethyl azoisobutyrate at 0°, the viscosimetric method[77] gave the value $k_p/k_t^{1/2} = 5.2 \times 10^{-4}$. It was assumed that $k_{dis} = 0$. The efficiency of the initiation was found to be only 0.05. For polymerisation in t-butyl alcohol[78] under the influence of diethyl peroxydicarbonate at 60° and ~50 atm, $k_p/k_t^{1/2} = 0.0182$. The initial rate depends on the concentration of initiator to the power 0.5. An independent method gave for the rate constant for the decomposition of the initiator in ethylene $k_{decomp} = 5 \times 10^{17} \exp(-33\,000/RT)$. The number-average molecular weight was determined ebulliometrically: the efficiency of initiation was close to 1.

Laita[79,80] obtained the values $k_p = 470$ and $k_t = 1.05 \times 10^9$ by the rotating-sector method at 83° in benzene solution; termination takes place by disproportionation of the radicals. Monoradical termination at initiator also takes place in the system with a rate constant of 185. The rate of initiation for the photodecomposition of azomethane was determined by the inhibition method and also from the number-average molecular weight of the polymer. The polymerisation at high pressures (750–2500 atm) was studied[81] in propane solution at 129° with di-t-butyl peroxide initiator. The rate of polymerisation is approximately proportional to the pressure and to the square root of the initiator concentration. With the assumption that the rate of decomposition of the initiator is independent of the pressure and that the efficiency of initiation is equal to 1, the values found for $k_p/k_t^{1/2}$ were 0.22 at 750 atm and 0.73 at 2500 atm.

Rabel and Ueberreiter[82] studied the polymerisation of ethylene "in bulk" for the photodecomposition of the same initiator at -20°. With the assumption that chain termination takes place by disproportionation, calculation by the method proposed by Schulz and coworkers[3] from the dependence of the viscosity-average degree of polymerisation on the reaction rate gave the value $k_p/k_t^{1/2} = 8.7 \times 10^{-4}$. The rotating-sector method gave $k_p/k_t = 4.1 \times 10^{-8}$. These values give $k_p = 18.6$ and $k_t = 4.55 \times 10^8$. Marked deviations have been observed[79,80,82] from the power $n = 0.50$ for the dependence on the intensity of initiation (up to $n = 0.76$); corrections were introduced by the method proposed by Burnett and Wright[83].

The data given for the constants for the elementary stages of the polymerisation of ethylene are contradictory. The values of $k_p/k_t^{1/2}$ from different papers do not lie on the Arrhenius straight line. This is apparently due to the low solubility of polyethylene in the monomer and also to the necessity to work under considerable pressures, different for different temperatures, in the determintion

of the constants "in bulk". The value of $k_p/k_t^{1/2}$ shows a marked pressure dependence at 750–2500 atm,[81] and it is not excluded that the dependence on pressure is preserved even at 20–60 atm. The nature of the solvent used in a number of experiments also appears to influence the value obtained for the constants.

Isoprene. The radical polymerisation of isoprene, like that of ethylene[78] (see above), stops at low degrees of conversion x as a result of consumption of the initiator. Treatment of these limiting conversion phenomena ("dead end") gives the equations[84]

$$-\ln(1-x_\infty)=2k_p\left(\frac{f(I)_0}{k_t k_{decomp}}\right)^{1/2}$$

and

$$\frac{\ln(1-x)}{\ln(1-x_\infty)}=1-e^{-\frac{k_{decomp}t}{2}},$$

which can be used to find the rate constant for the decomposition of the initiator k_{decomp} from the polymerisation kinetic curves. If the efficiency of initiation f is found by an independent method, the above equations can be used to determine $k_p/k_t^{1/2}$.

For the polymerisation of isoprene[85] "in bulk" at 60–90°, this method gave $k_p/k_t^{1/2} = 1\times10^4\exp(-9800/RT)$. Taken with the value $k_p = 1.2\times10^8\exp(-9800/RT)$, determined by emulsion polymerisation[86], this gives $k_t = 1.34\times\times10^8$.

2,3-Dimethylbuta-1,3-diene. Emulsion polymerisation in the range 5–60°[87] gave the value $k_p = 8.9\times\times10^7\exp(-7000/RT)$.

Maleic anhydride. The rate of free-radical polymerisation[88] "in bulk" at 74.5° with benzoyl peroxide is directly proportional to the square root of the initiator concentrations. The length of the polymer chains gives the value $k_p/k_t^{1/2} = 0.0092$.

The reactions of telomerisation and the addition of radicals across the double bond of vinyl compounds are similar to polymerisation reactions. In recent years a number of kinetic studies have been made of the reactions involved in the addition of bromotrichloromethane to certain monomers and various compounds containing a double bond. The method used to determine the rates of the elementary steps in these reactions is basically the same as that used for polymerisation reactions. Photochemical reactions involving CCl_3Br are convenient since no sensitising agent is required. CCl_3Br decomposes to $CCl_3^\cdot$ and $Br_3^\cdot$ radicals under the influence of ultraviolet light.

The photochemical addition of bromotrichloromethane to vinyl compounds (denoted M) with the formation of the 1:1 adduct involves the following elementary steps[89]:

$$CCl_3Br+h\nu \xrightarrow{I} CCl_3^\cdot + Br^\cdot \quad (22)$$

$$CCl_3^\cdot + M \xrightarrow{k_2} CCl_3M^\cdot \quad (23)$$

$$CCl_3M^\cdot + BrCCl_3 \xrightarrow{k_3} CCl_3MBr + CCl_3^\cdot \quad (24)$$

$$CCl_3^\cdot + CCl_3^\cdot \xrightarrow{k_4} C_2Cl_6 \quad (25)$$

$$CCl_3^\cdot + CCl_3M^\cdot \xrightarrow{k_5} \text{products} \quad (26)$$

$$CCl_3M^\cdot + CCl_3M^\cdot \xrightarrow{k_6} \text{products} \quad (27)$$

Kinetic analysis of the scheme by the method of quasi-steady states gives the equation

$$V_{st} = -\frac{d[M]}{dt} = \frac{k_2 I^{1/2}[M]}{k_4^{1/2}} \times \frac{1}{\sqrt{1+\frac{k_6}{k_4}\left(\frac{k_2}{k_3}\right)^2\left[\frac{[M]}{[CCl_3Br]}\right]^2+\frac{k_2k_5[M]}{k_3k_4[CCl_3Br]}}}, \quad (28)$$

which becomes Eqn. (4) with $k_p = k_2$ and $k_t = k_4$, if $\alpha = [M]/[CCl_3Br]$ is sufficiently small. The steady-state rate can also be expressed in terms of the CCl_3Br concentration and then the expression, analogous to (29), becmes Eqn. (4) with $k_p = k_3$ and $k_t = k_6$ if $1/\alpha$ is sufficiently small. Thus the values of k_2 and k_4 are determined in experiments with an excess of CCl_3Br and k_3 and k_6 are determined in an excess of M. The applicability of Eqn. (4) here is determined experimetanlly from the linear dependence of the steady-state rate on the concentration of M or CCl_3Br respectively, and also from the dependence of V_{st} on the square root of the intensity of illumination.

The reaction of CCl_3Br with cyclohexene. Melville and coworkers[90] obtained the following values for the constants in a large excess of CCl_3Br at 30–50°: $k_2 = 4\times10^5\exp(-3400/RT)$, $k_4 = 1\times10^8$, and $E_4 = 0$. The ratio k_2/k_4 was determined by the rotating-sector method and the rate of initiation was found from the rate of consumption of the inhibitor tetrachloro-*o*-quinone.

These determinations were repeated[24] at 25° from the adiabatic increase in temperature and the value $k_2/k_4 = 2.1\times10^{-5}$ was obtained. The effective activation energy for the photochemical reaction $E_2 - \frac{1}{2}E_4 = 3.5$ kcal, which agrees with Melville's data. The determination of the rate of initiation by the usual method involving the introduction of an inhibitor into the photoinitiated reaction may lead to errors, since tetrachloro-*o*-quinone absorbs light strongly even at the low concentrations required for measurement of the rate of initiation. The value $k_2/k_4^{1/2} = 0.87\times10^{-2}$ was obtained at 60° from the rate of decomposition of inhibitor in the reaction initiated by the thermal decomposition of azoisobutyronitrile, and agreed with the value calculated from the rate of decomposition of the initiator for $f = 0.40$. The activation energy can be used to calculate $k_2/k_4^{1/2}$ at other temperatures. The values $k_2 = 1100$ litre mole^{-1} s^{-1} and $k_4 = 0.52\times10^8$ litre mole$^{-1}\times\times$ s^{-1} were obtained in this way. That the values of $k_2/k_4^{1/2}$ determined by Melville and coworkers[90] and by Bagdasar'yan and Revzin[24] differ by a factor of six is evidently due to some inaccuracy in the former determination[90] (see our paper[24] for more detail).

It was shown[91] that the reaction of CCl_3Br with cyclohexene involves not only the addition of the $CCl_3^\cdot$ radical across the double bond but also the removal of an α-hydrogen atom:

$$CCl_3^\cdot + C_6H_{10} \xrightarrow{k_7} CHCl_3 + C_6H_9^\cdot \quad (29)$$

The ratio k_2/k_7 was recently determined[92] for a number of hydrocarbons. For cyclohexene, $k_2/k_7 = 1.20$ at 78° and 1.85 at 40°. From these two points, $E_2 - E_7 = -2.5$ kcal$\times\times$ mole^{-1}, so that $E_7 = 6.0$ kcal mole^{-1}. Extrapolation to 25° gives $k_2/k_7 = 2.28$, that is $k_7 = 483$ litre mole^{-1} s^{-1}‡.

‡ Bagdasar'yan and Revzin[24] give slightly different figures for k_2 and k_7, since the experimentally-determined value of k_2 was erroneously taken[24] as the sum of the rate constants for reactions (23) and (29). This point was brought to our attention by A.N. Pravednikov.

For an excess of cyclohexene, Melville and coworkers[93] obtained the values $k_3 = 63.8$, $E_3 = 4.5$ kcal mole^{-1}, $k_7 = 4 \times 10^7$, and also $k_5 = 5.7 \times 10^8$. The activation energy for termination $E_6 = E_5 \simeq 0$.

The reaction of CCl_3Br with hept-1-ene was studied[24] at different reagent ratios in the range 15–40°. The rate of initiation in an excess of CCl_3Br was assumed to be the same as in the reaction with cyclohexene, and the rate of initiation in an excess of hept-1-ene was calculated at 60° from the rate of the thermal decomposition of the initiators. The adiabatic increase in temperature gave the values $k_2 = 2.3 \times 10^9 \exp(-7000/RT)$, $k_3 = 2.48 \times 10^8 \exp(-8500/RT)$, $k_4 = 1.38 \times 10^8$, and $k_6 = 1.03 \times 10^6$ litre mole^{-1} s^{-1}; $E_4 = E_6 \simeq 0$.

A curious feature is the anomalously low value, which is difficult to explain[95], of the rate constant for addition to cyclohexene shown both by the $CH_3^\bullet$ radical and by the $CCl_3^\bullet$ radical. The rate of removal of hydrogen from cyclohexene, however, is apparently quite "normal": by extrapolating k_2 for cyclohexene to 77.8° and making use of the value $k_2/k_7 = 1.20$ for this temperature[92], we obtain for cyclohexene $k_7 = 2200$; similar calculations for hept-1-ene give the value $k_7 = 2400$. Thus the difference in the rates of removal of hydrogen k_7 by the $CCl_3^\bullet$ radical from cyclohexene and hept-1-ene is insignificant and confirms the observation, found for other radicals, that the reactivity of secondary hydrogen atoms is approximately the same for all alkenes and cycloalkenes.

For the reaction of CCl_3Br with n-butyl vinyl ether[94], $k_2 = 3.16 \times 10^{10} \exp(-7700/RT)$, and for the reaction of CCl_3Br with phenyl vinyl ether, $k_2 = 2.0 \times 10^4$ at 25° (the value of k_4 was taken as 1.0×10^8).

The value $k_2 = 3240$ litre mole^{-1} s^{-1} has been reported[92] for the addition of $CCl_3^\bullet$ to methylallyl acetate at 30°; the activation energy for this reaction is 7.74 kcal mole^{-1}.

For the addition to vinyl acetate the rotating-sector method[93] gave $k_2 = 1120$ at 30° and $E_2 = 6.1$ kcal mole^{-1} in the same laboratory; later, Bengough and Thomson[96] determined the rate of initiation from the rate of consumption of diphenylpicrylhydrazyl or from the duration of the induction period in different solutions at 25° and obtained the value $k_2 = 795$–2410, depending on the method used to determine I. These small values for vinyl acetate are even more surprising than those for cyclohexene, since the rate of addition of $CCl_3^\bullet$ to other rapidly polymerising monomers (styrene, methyl methacrylate) is greater by approximately one order of magnitude. The telomerisation of bromotrichloromethane with a large excess of vinyl acetate[97] leads to the formation of telomers containing different numbers of monomer units for every CCl_3 group. From their data[97], the authors concluded that the value obtained by Melville and coworkers[93] for the rate constant for the removal of the Br atom from CCl_3Br by the $CH_3COOCHCH_2CCl_3^\bullet$ radical at 30°, $k = 2740$, is clearly too low. For other substances with different structure, including active monomers (see below), however, this quantity has values in the range 13–400, that is, the value of k_3 for vinyl acetate is greater by one order of magnitude than the values for other substances.

Robb and coworkers studied the mechanism and kinetics of the photochemical telomerisation of bromotrichloromethane with styrene[98,99] and methyl methacrylate[100]. The rate of initiation was determined from the duration of the induction period in the presence of diphenylpicrylhydrazyl, and the lifetime of the free radicals was determined by the rotating-sector method. The reaction rate is proportional to the square root of the intensity of illumination.

The following values were found for the rate constants of the dimeric and trimeric teloradicals at 30°:[99]

	k_a	k_p	k_t
$[(C_6H_7)_2CCl_3]^\bullet$	$4.4 \cdot 10^3$	56.8	$5 \cdot 10^8$
$[(C_6H_7)_3CCl_3]^\bullet$	$4.3 \cdot 10^3$	1.56	$1.6 \cdot 10^8$

The symbols for the constants have their usual significance: k_3 is the constant for the removal of a bromine radical from CCl_3Br, k_p the constant for the addition to a molecule of monomer, and k_t the constant for recombination of the radicals. When the number of monomer units in the telomer chain is greater than or equal to 4, the value of k_p again increases to the usual value for the polymerisation of styrene.

For the reaction of methyl methacrylate with trichlorobromomethane[100], the rate constants for the telomeric radicals $[(MMA)_nCCl_3]^\bullet$ at 30° have the following values:

n	k_a	k_p
3	13.3	160
4	8.34	37.9
5	330	281

The termination rate constant $k_t = 1.6 \times 10^7$ is independent of the value of n.

Thus the systems studied show a minimum reactivity for the trimer for styrene and the tetramer for vinyl acetate (according to the data of Bengough and Thomson[97], examined critically by Robb and Senogles[100]) and methyl methacrylate. The same phenomena were observed in the telomerisation of esters of acrylic acid with lower thiols[101]. The reduced reactivity of the trimers and tetramers was attributed to the fact that, as a result of the steric conditions here, the CCl_3 (or SH) group attached to the first unit is in direct proximity to the C atom carrying a free valency, and reacts with it. Moreover, the influence of the CCl_3 group on the activity of the radical decreases with increase in the length of the telomeric radical chain. The reactions of telomers show particulary clearly that the rate constants for propagation and termination of the chain, determined in polymerisation, refer, strictly speaking, only to the reactions of sufficiently large polymeric radicals containing more than four units. In polymerisation reactions, the difference in the rates of reaction for 2- and 3-unit or longer polymeric radicals is smaller, however, than that for telomerisation reactions.

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FEATURES OF THE KINETICS OF CHEMICAL REACTIONS OF HIGH-MOLECULAR-WEIGHT COMPOUNDS

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I. INTRODUCTION

The study of the kinetics of homogeneous reactions of macromolecules has recently received much attention from several investigators [1-37]. The interest in this problem is due to the search for ways of controlling the chemical changes in polymers and of carrying out directed reactions to obtain chemical derivatives with desired properties.

By comparing the kinetic parameters of reactions of functional groups included in the polymer chain with the analogous parameters of the same groups in low-molecular-weight compounds, it is possible to suggest a series of factors which lower the pre-exponential term of the Arrhenius equation for large molecules [1]. Firstly, from the kinetic theory, with increase in the dimensions (mass) of the molecule the rate of the Brownian movement of the molecules falls. Secondly, the high viscosity of the polymeric solutions decreases the number of collisions of the reacting groups. Thirdly, there is the great steric factor due to the screening of the functional groups by coiling of the polymeric chains.

When there is regular attention of the functional groups in the polymeric chain, the interaction of neighbouring groups (of two which have not reacted or which have reacted with those which have not yet entered into reaction, etc.) can affect the energy of activation.

This review shows the influence of the inclusion of a functional group in a polymeric chain and the interaction of regularly alternating functional groups on the kinetic parameters of reactions of macromolecules.

II. INFLUENCE OF THE INCLUSION OF A FUNCTIONAL GROUP IN A POLYMERIC CHAIN ON THE KINETIC PARAMETERS FOR THE REACTIONS OF THIS GROUP

There are many experimental results which show that the inclusion of a functional group in a polymeric chain does not significantly change either the activation energy or the pre-exponential term of the Arrhenius equation for reactions of this group with low-molecular-weight agents. Thus, Fuoss and coworkers [2], in studying the formation of quaternary salts of poly(vinylpyridine) and low-molecular pyridine compounds obtained the following constants for reaction rates and activation energies (Table 1).

The reaction was effected in tetramethylene sulphone; the alkyl halide used was n-butyl bromide.

TABLE 1. Kinetic parameters of the Menshutkin reaction for poly(vinylpyridine) and low-molecular-weight pyridines.

	$10^3 K_2$			E_a
	25°	50°	75°	
Pyridine C_5H_5N	0.463	3.70	23.1	16.04
4-Isopropylpyridine $C_3H_7C_5H_4N$	0.904	6.95	39.7	15.6
Poly(vinypyridine) (first stage of reaction)	0.64	5.4	29.4	15.7
4-Picoline $CH_3C_5H_4N$	0.83	6.58	40.1	15.95

Table 1 shows that the inclusion of pyridine in the polymeric chain affects neither the activation energy nor the reaction rate constant. Analogous results were obtained when propylene carbonate [4 methyl-1,2-dioxolan-2-one (Ed. of Translation)][3], 2,4-dimethylsulpholane [2,4-dimethyltetramethylene sulphone (Ed. of Translation)][4] or a mixture of propylene carbonate and diphenyl ether [5] was used as solvent.

Loucheux and Banderet[6] investigated the kinetic parameters of the reactions of macromolecules with one or several groups. In the range of functional group concentrations from 10^{-6} to 10^{-8} (per 1 cm^3) the rate of reaction of monoanhydride with aniline is the same for both the functional group of a macromolecule and the low-molecular-weight anhydride. The rate of reaction is independent of the viscosity of the solution even beyond the gelling point.

Moens and Smets[7] found that the rate constants and the Arrhenius parameters for the alkaline hydrolysis of poly(diethylacrylamide) were identical with those for diethyl isobutyramide (Table 2).

TABLE 2. Alkaline hydrolysis of amides.

	$10^4 K_{1,OH}$, s^{-1}			E_a	$\log PZ$
	60°	70°	80°		
Poly(diethylacrylamide)	0.14	0.415	1.15	22.05	9.47
Diethylisobutyramide	0.20	0.51	1.24	21.70	9.07

In the alkaline hydrolysis of amides[8] the Arrhenius parameters for polyacrylamide and isobutyramide are identical (E_a = 14.16 kcal $mole^{-1}$ and $\log PZ$ = 5.63 for the first stage of the hydrolysis of polyacrylamide and E_a = 14.2 kcal $mole^{-1}$ and $\log PZ$ = 5.56 for the hydrolysis of isobutyramide).

Similar results are obtained in the acid of poly-(*N*-ethylacrylamide) and *NN'*-diethylisobutyramide: the activation energy for the first is 24.6 kcal $mole^{-1}$ and the number of effective collisions was characterised by $\log PZ$ = 9.49; for the model low-molecular-weight compound E_a = 23.7 kcal $mole^{-1}$ and $\log PZ$ = 9.20.

Conix and Smets[9] obtained the following results in the hydrolysis of low- and high-molecular-weight lactams (Table 3).

TABLE 3. Hydrolysis of lactams.

	E_a, kcal $mole^{-1}$	$\log PZ$
Poly-(*N*-vinylpyrrolidone)	25±1	11.7
N-Isopropyl-2-methylpyrrolidone	27±0.5	12.3
Copolymer of vinylpyrrolidone and maleic acid (68 : 32)	16±1	6.3
Pyrrolidone-*N*-acetic acid	17±0.5	7.3

By studying the acetylation of cellulose and the reverse reaction of hydrolysis, Hiller[10] showed that the rate of reaction and activation energy in the acetylation of the primary hydroxyl groups in cellulose were of the same order as for the analogous reactions of butanol.

Salomon and coworkers[11,12] note that the activity of the chloride of natural rubber, which contains 20–30% allyl chloride, with respect to aniline is identical with that of low-molecular-weight allyl chlorides.

Losev and Trostyanskaya[13] state that in solutions, reaction between a polymer and a monomer proceeds at a rate similar to that for reaction of two low-molecular-weight substances.

Billmeyer[1] explains as follows the similarity between the kinetic parameters of the reactions of the functional groups in polymers and low-molecular-weight compounds in polycondensations.

Firstly, the mobility of the functional groups in a polymeric chain is considerably greater than the mobility of the chain itself. The functional groups move easily within a considerable region as a result of the change in configurations of the neighbouring parts of the chain. The frequency of the collision of these groups with their neighbours is comparable with the frequency of the collisions of low-molecular-weight compounds.

Secondly, in addition to the lower rate of diffusion, due to the high viscosity of the solutions of polymers and the increase in the time needed for the approach of the reacting groups, there is also an increase in the time for these groups being together and consequently in the effective collision number.

Thirdly, a screening effect can appear only in dilute solutions; at high concentrations the chains of the macromolecules are so greatly entangled that the chain proper, from the point of view of the screening of the functional groups forming part of it, has no advantage over the chains of other molecules.

Probably the same factors lead to the similarity between the kinetic parameters of the reactions of functional groups in polymers and in low-molecular-weight compounds as cited above.

III. INFLUENCE OF THE INTERACTION OF FUNCTIONAL GROUPS IN A POLYMERIC CHAIN ON THE REACTION KINETICS

The similarity of the kinetic parameters of the reactions of functional groups in high polymers and low-molecular-weight compounds can be upset if during the reaction the molecule of high polymer becomes charged and the charged groups are situated beside functional non-reacting groups.

Fuoss and coworkers[14] investigated the kinetics of the Menshutkin reaction for poly(vinylpyridine). The general kinetics of the reaction do not correspond with the kinetics of the reactions of low-molecular-weight pyridines. As the pyridine group forms part of the molecular chains, the successive reaction to form quaternary salts should take place at small distances from the groups that have already reacted. In solvents of high dielectric constant a considerable proportion of the bromide ions leaves the site of the pyridinium ions, creating a positive electric field of high intensity at the polymeric chain. As a result, after one-third of all the groups have reacted each remaining group will have an average of one charged neighbouring group, and when one-half of all the groups have reacted the remaining groups will have two charged neighbour groups. Thanks to the field of the positive charge of the nitrogen which reacted first, the rate constant falls to one-tenth of its initial value at the group of the neighbouring nitrogen.

Moens and Smets[7] showed the influence of the accumulation of charge on a macromolecule during the course of

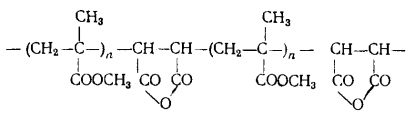
the reaction on the kinetic parameters of the alkaline hydrolysis of polyacrylamides. The hydrolysis can be divided into two clearly defined stages, the first being rapid, with a rate similar to that for the hydrolysis of the model low-molecular-weight compound, and the second being slow. During the initial stage the reaction is first order, but after reaching ~ 40% conversion the rate constant falls.

At low degrees of hydrolysis the molecule has a convolute configuration. At ~ 40% conversion the chain is uncoiled owing to electrostatic repulsion of the carboxyl groups present in a single molecule. The accumulation of charge on the macromolecule leads to an increase in the rigidity of the chain, a change in its configuration, and a diminution in the rate constant.

Kargin and coworkers [15] showed the influence of the electrostatic factor on the kinetic parameters of the hydrolysis of ethyl acetate, which is catalysed by poly(styrenesulphonic acid) (PSSA). Toluenesulphonic acid (TSA) served as a low-molecular analogue of PSSA. In the presence of PSSA the rate of hydrolysis was 1.3–1.8 times as great. The difference in the rates of reactions catalysed by PSSA and by TSA increases as the catalyst concentration is reduced.

The high activity of PSSA is explained by the increase in the concentration of protons (in the form of oxonium ions H_3O^+) close to the polymer chains. In the oxonium cloud around the macroanion the activity coefficients of the H_3O^+ ions are greater than in the TSA solution, where the H_3O^+ ions are distributed uniformly throughout the entire volume. During this, the increase in the rate of hydrolysis in the oxonium cloud is not compensated by the fall in the reaction rate in the regions of the solution denuded of H_3O^+ ions. Naturally, the more dilute the solution the more marked this effect.

Loucheux and Banderet [6] investigated the reaction of aniline with a copolymer of methyl methacrylate and maleic anhydride in which the anhydride groups were not adjacent:



The greater the number of anhydride groups in the macromolecule, the less the rate of reaction, all other conditions being equal. This occurs because, in a non-polar solvent (benzene), the macromolecule with a low concentration of anhydride groups mixes well with the solvent. An increase in the number of anhydride groups in the macromolecule increases its polarity, which leads to a complication of the polymeric chain into more intimate tangles. As a result, the anhydride groups become less accessible and the rate of reaction decreases.

The kinetic similarity of the reaction of polymers and low-molecular-weight compounds fails when an intramolecular reaction is possible for a polyfunctional polymer. Arcus [16] showed this by the example of the alkaline hydrolysis of poly(methyl methacrylate). At the start of the reaction the polymer contains only amido-groups which are mono-functional. During the reaction carboxyl groups appear as well as the amido-groups, and because both are fixed in a polymeric chain hydrogen bonds are formed between them, increasing the activation energy for hydrolysis of the amido-groups, as a result of which the reaction rate is sharply depressed. When each amido-group has two carboxyl groups as neighbours, the reaction ceases. Under those conditions the low-molecular-weight amides are hydrolysed to completion. Smets [8] considers that it is not hydrogen bonds but electrostatic repulsion and steric hindrance which lead to the progressive retardation of the alkaline hydrolysis of the alkaline hydrolysis of polyacrylamide.

Moens and Smets [7] observed the effect of intramolecular chemical reaction of functional groups on the kinetic parameters of their reactions by the example of the acid hydrolysis of poly(vinylamides). They thought that the hydrolysis was accompanied by imidisation, which lowers the reaction rate and raises the activation energy by 3.5 kcal.

Smets and Petit [38] observed an increase in the activation energy due to the association of functional groups in a monofunctional polymer. Thus in the acetylation of poly(vinyl alcohol) at a sulphuric acid concentration of 0.5 N and 0.05 N the activation energy was 9.5 and 15 kcal respectively. The increase in E_a by 5.5 kcal in the second case is due to the association of hydroxyl groups.

In polyfunctional polymers the kinetic parameters can be affected by catalytic action shown by one functional group to another.

Moens and Smets [7] compared the alkaline hydrolysis of polyacrylamide with the hydrolysis of low-molecular-weight amides (Table 4).

As Table 4 shows, the rate of reaction of the functional groups in the polymer is greater than that in the low-molecular-weight compounds. Morawetz explains this by the specific catalysis of the carboxyl groups in the first stage of the reaction.

TABLE 4. Hydrolysis of amides.

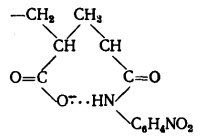
	$10^4 K_2$, OH, mole^{-1} s^{-1}					E_a	log PZ
	55°	65°	70°	75°	85°		
Polyacrylamide	6.66	—	18.6	—	38.8	13.7	5.99
Isobutyramide	1.16	2.36	—	3.95	—	14.2	5.56
Glutaramide	—	3.80	—	6.94	12.7	14.8	6.01
Acrylamide	1.47	3.70	—	6.66	13.8	16.6	7.24
Propionamide	5.24	9.98	—	17.7	—	14.6	6.10

The nature of the intramolecular catalysis of hydrolytic reactions was studied in detail by Bender and coworkers using the example of acid and alkaline hydrolysis of phthalamic acid [39,40] and the hydrolysis of methyl phthalate [41]. Kinetic comparison of several low- and high-molecular-weight compounds showed a great difference between the intramolecular and intermolecular hydrolysis [42].

Smets and Petit [38] observed the catalytic action of a hydroxyl group situated directly next to an acetyl group in the hydrolysis of poly(vinylacetal).

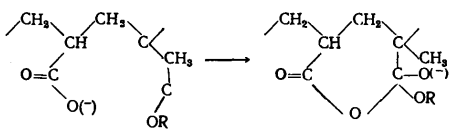
Schaefgen and Sarasohn [17] carried out the quantitative thermal decomposition of poly(butyl acrylate) into 2-methylprop-1-ene and poly(acrylic acid). Initially the reaction follows a statistical law. When 9.4 ± 2% has been converted, there is a rapid autocatalytic splitting-off of ester groups owing to the action of neighbouring carboxylic groups.

The investigations of Morawetz and coworkers [18,19] showed that the introduction of methacryl-*p*-nitroanilido--groups into a polyacid molecule makes these groups a thousand times more stable to sodium hydroxide, in comparison with the *p*-nitroanilides of trimethylacetic and glutaric acids. The stabilisation results from ring formation:



from an increase in the steric effect, and from an increase in the electrostatic repulsion. This explanation is confirmed by the accelerating effect of the addition of small quantities of Ba^{2+} ions, which, by bonding the carboxylate groups, free the anilide groups.

The hydrolysis of *p*-nitrophenylmethacrylic groups, introduced into the chain of poly(acrylic acid) to the extent of ~ 1%, goes a million times faster than the hydrolysis of *p*-nitrophenyl trimethylacetate [20,21]. Morawetz explains this by the selective catalytic action of a neighbouring carboxylate ion with the formation of an intermediate complex:

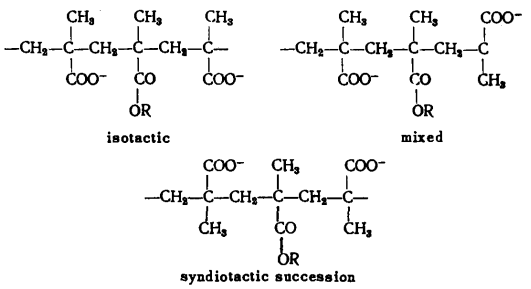


Smets and De Loecker [22] investigated the hydrolysis of copolymers of methacrylic acid and methyl methacrylate, at various ratios of the components. Under similar conditions the copolymer of methyl methacrylate and vinylpyrrolidone is hydrolysed 1000 times more slowly since with the latter the catalytic action of carboxyl groups is absent.

Smets and Hesbain [23] studied the hydrolysis of polyacrylamide and of copolymers of acrylamide and acrylic acid in an acetate buffer solution. The presence of the carboxyl group along with the amide in the copolymer increases the rate of hydrolysis three thousand times compared with the rate of hydrolysis of polyacrylamide.

The kinetic parameters of functional groups in a macromolecule are greatly affected by the stereoregularity of their distribution, when the polymer is polyfunctional — or when the reacting groups display a catalytic action on neighbouring functional groups, not taking part in the reaction. Thus, Glavis [24] showed, by the example of the alkaline hydrolysis of poly(methyl methacrylate)s of different tacticity, that the standard (atactic) and syndiotactic polymers are hydrolysed comparatively slowly but the isotactic polymers very rapidly and to a much greater degree. Smets [8] carried out the hydrolysis of atactic and isotactic copolymers of methacrylic acid with its ester (72% acid). The isotactic copolymer is hydrolysed 10–15 times more rapidly than the atactic and to a greater extent (40% instead of 20%).

The hydrolysis of a copolymer of methacrylic acid with 1–2% *p*-nitrophenyl methacrylate with isotactic succession of the carboxyl and ester groups is 12 times faster than that for a mixed succession [25]:



Smets and De Loecker [26,27] investigated the hydrolysis of copolymers of methacrylic acid with methyl methcrylate of the same chemical structure but different tacticity. The rate constants of the hydrolysis of a syndiotactic copolymer were four to five times those for the atactic. The syndiotactic copolymer is hydrolysed in a single stage, after which the reaction stops; the atactic copolymer in two stages with a ratio of the rates $K_1 : K_2 = 1 : 6$.

A comparison with the hydrolysis of a copolymer of methylmethacrylic acid and *N*-vinylpyrrolidone shows clearly that the ester and carboxyl groups interact with one another, which leads to a drop in the energy of activiation from 23 to 16 kcal.

Chapman [28] studied the acid hydrolysis of very crystalline isotactic and amorphous atactic poly-(*NN*-dimethylacrylamide)s. The isotactic polymer is hydrolysed more rapidly, since owing to the intramolecular nature of the hydrolysis the activation energy is reduced from 29 to 22.6 kcal. On the basis of his investigations Chapman proposes a method for determining the degree of tacticity by hydrolytic measurements.

Smets and Van Humbeeck [29] studied the hydrolysis of copolymers of acrylic acid and ethyl ethacrylate containing 50, 67, 77, and 85% of the acid. The hydrolysis rate is directly proportional to the concentration of the acid–ester–acid triad and the isotactic polymer is hydrolysed three to five times more rapidly than the atactic, and to a greater extent. The hydrolysis of copolymers of acrylic acid and t-butyl acrylate and of polymers of poly-(t-butyl acrylate) is independent of their stereoregularity, since the intramolecular interaction of the functional groups is ruled out by the strong steric effect.

Fujii and coworkers [30–32] showed the influence of stereoregularity on the kinetic parameters of the reactions of polymers by the example of hydrolysis of poly(vinyl acetate) and the acetalisation of poly(vinyl alcohol).

The kinetic similarity of the reaction of polymers and of low-molecular compounds breaks down when the functional groups or double bonds can bring about electronic interaction along the polymeric chain.

Cunneen [42–44] showed a diminution in the reactivity of double bonds relative to electrophilic agents on going from low-molecular monoalkenes to 1,5-polyenes, for example, of the reaction of polyisoprene and cyclohexene with ethanethiol, 3-methylbutane-1-thiol, thiophenol, thioglycollic acid [43], propane-1,3-dithiol and hexane-1,6-dithiol [44], and thioacetic and chlorothioacetic acids [45]. The reactivity is reduced in the order: cyclohexene > dihydromyrcene > > squalene > natural rubber.

We have found complete inertness of *cis*- and *trans*-polyisoprenes towards ethyl thioglycollate, whereas its addition to isopentene proceeds very readily [46].

Bateman and coworkers [47] note a fall in the reactivity of double bonds in polyisoprene compared with low-molecular-weight alkenes in hydrogenation.

We assume that the fall in reactivity of double bonds in 1,5-polyene systems in relation to electrophilic reagents is connected with the interaction of double bonds regularly alternating in the 1,5 positions. We have already considered the mechanism of this interaction [47]. Such an interaction of double bonds in diene polymers leads to the development of a series of reactions of these polymers by an intramolecular chain mechanism [46,48].

Alfrey and Lloyd [33] showed an intramolecular chain mechanism in the dehydrochlorination of poly(vinyl chloride). The act of reaction in one monomer unit converts a neighbouring unit into an allyl structure with an enhanced tendency to dehydrochlorination, which should lead to the chain development of the process and to the formation of a block of conjugated bonds.

There are several theoretical works on the kinetics of reactions of macromolecules in which the mean number of reacting functional groups is determined as a function of time under the condition that the reactivity of each group depends on how many of the neighbouring groups (one, two, or none) have already reacted [14,33-37].

The features noted do not, of course, exhaust all the specific characteristics of the kinetics of the reactions of polymers. The tasks of future investigations in this interesting and little studied field are the accumulation of information on the influence of the solvent on the course of the polymeric reactions, and also on the influence of secondary structures in solutions of polymers on the topochemical and kinetic features of the reactions.

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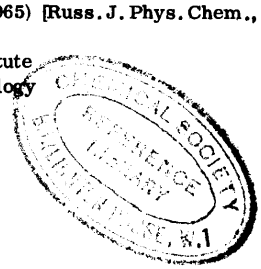

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MEASUREMENT OF TRANSPORT NUMBERS IN AQUEOUS SOLUTIONS OF ELECTROLYTES

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I. INTRODUCTION

Problems arising in the measurement of the transport numbers and mobilities of ions in electrolyte solutions have been the object of many experimental and theoretical investigations[1-4]. The development of experimental techniques was particularly vigorous at the beginning of the present century, when the moving boundary method and the e.m.f. method achieved a popularity as wide as that of the Hittorf method. Since the late 1940's, several new procedures have been developed intensively, and have helped to provide many experimental data whose effect has been to increase our understanding of the transport numbers and mobilities of ions in solutions of various chemical compounds.

The most important characteristic of the motion of ions in solutions is ionic mobility. The mobility is a function of all the parameters of the solution, and is defined as the velocity of the ions under the influence of a unit potential gradient (1 V cm^{-1}). The ability of an electrolyte to carry an electric current, *i.e.* the electrical conductivity of the electrolyte, is determined by the total charge and by the mobility of the ions. The total current passing through a unit cross-section of a solution containing a mixture of various ions is given by

$$j = F \sum_i c_i z_i u_i , \qquad (1)$$

where c_i, z_i, and u_i are the concentration, the charge, and the mobility of the ions of the i-th kind, respectively, and F is Faraday's constant.

The fraction of the current carried by ions of the i-th kind is called the transport number of those ions, and can be expressed in the form

$$T_i = \frac{u_i z_i c_i}{\sum_i u_i z_i c_i} . \qquad (2)$$

Obviously, the sum of the transport numbers of all kinds of ion present in solution is

$$\sum_i T_i = 1. \qquad (3)$$

In the simplest case of a binary electrolyte, dissociating into two ions ($MA \rightleftharpoons M^+ + A^-$), of mobility u_{M^+} and u_{A^-} respectively, the transport numbers are

$$T_{M+} = \frac{u_{M+}}{u_{M+} + u_{A-}}, \quad T_{A-} = \frac{u_{A-}}{u_{M+} + u_{A-}}, \tag{4}$$

since the equivalent concentrations of the ions are equal. Ionic mobilities can be determined experimentally by measuring the velocity of the ions and the electrical potential gradient. Lodge[5] and Whethem[6] were the first to attempt this measurement, but they experienced great difficulty in measuring the electric field (and therefore also the mobility) with adequate precision. Later workers determined mobility values by calculation, from measured transport numbers, and from the electrical conductivity of the solutions. Electrical conductivity data are now available for a large number of electrolytes, but data relating to transport numbers are far less plentiful. This is because transport number measurements present more serious experimental difficulties.

All existing methods for measuring transport numbers rely on the displacement of atoms of a given kind as a means of monitoring the motion of charges. In fully dissociated solutions, which includes most dilute solutions, the displacements of atoms and charges are identical, and existing methods of measurement give a correct assessment of the motion of ions in solutions. A more complicated situation exists when a given substance can contribute to the composition of both the anions and the cations. There is ample experimental evidence for the formation of ion pairs in solution, and also of groups of three ions (ion triplets)[7,8]. Complex formation very often takes place in electrolyte solutions[9-11]. All these effects cause the experimentally measured transport numbers to differ from the values given by Eqn. (4). If the M atoms in a solution of MA can enter into the composition of both the cations and the anions, the value of the transport numbers obtained experimentally can be expressed as

$$T_M = \frac{\sum_i^n z_i u_{ci} c_{ci} p_{cMi} - \sum_i^m z_i u_{ai} c_{ai} p_{aMi}}{\sum_i^n z_i u_{ci} c_{ci} + \sum_i^m z_i u_{ai} c_{ai}}, \tag{5}$$

where u_{ci} and c_{ci} are the mobility and the concentration of cations of the i-th kind, u_{ai} and c_{ai} the mobility and the concentration of anions of the i-th kind, p_{cMi} is the number of M atoms included in the composition of the i-th cationic component, and p_{aMi} the number of M atoms included in the composition of the i-th anionic component.

The summation is carried out over all kinds of cation (n) and of anion (m). It is evident that the case where $\sum_{i=1}^{m}$ is greater than $\sum_{i=1}^{n}$ corresponds to anomalous values of the transport number.

Thus, the experimentally measured transport numbers are a measure of the ratio of the resulting flux of atoms of the substance M to the total flux of charged species[12].

The interactions between ions and the solvent lead to the formation of solvation (hydration) shells around the ions, which move in the electric field together with the ions[13-15]. The difference in degree of solvation and in mobility between cations and anions results in a net transfer of solvent in one direction, which has given rise to the concept of apparent and true transport numbers. Existing methods of measuring transport numbers use the solvent as the system of coordinates, and do not take account of the motion of solvent with the ions. Transport numbers measured in this way are the apparent (or, as they are often called, Hittorf) transport numbers. To measure true transport numbers, the system of coordinates is based on the solution as a whole[16,17], so that the preferential motion of the solvent is automatically compensated.

Experimental methods for measuring apparent transport numbers can be divided into three groups: (a) Hittorf's method; (b) methods based on the measurement of the e.m.f. of galvanic cells; (c) methods based on the observation of ionic boundaries.

The present review deals with existing methods of measuring apparent transport numbers of ions in aqueous solutions of electrolytes, the main emphasis being on methods developed relatively recently. Generalised experimental data on transport numbers in aqueous solutions of electrolytes are presented. Problems arising in the determination of true transport numbers and in measurements in non-aqueous electrolytes are not considered.

II. HITTORF'S METHOD

The principle of the method was first proposed by Hittorf[18-25] in 1853. It is most conveniently discussed by considering a binary electrolyte which dissociates by the reaction $MA \rightleftharpoons M^+ + A^-$. Fig. 1 shows an electrolytic cell for transport number measurements. If no secondary chemical reactions occur at the electrodes during electrolysis, and ions disappear from the cathodic compartment V_c by being discharged, after time t the loss of M^+ cations from the volume V_c will be

$$P_{M+} = \frac{It}{F}, \tag{6}$$

where I is the current passing through the cell.

From the direction of the anode, a flow of M^+ cations enters V_c through the cross-section S:

$$I = \frac{T_{M+}}{F} \cdot \frac{\partial q}{\partial t} + DS\frac{\partial c}{\partial x}, \tag{7}$$

where T_{M^+} is the transport number of the M^+ ions, q the quantity of electricity carried by the cations, t the time,

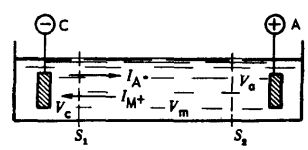

Fig. 1. Schematic diagram of an electrolytic cell for the measurement of transport numbers by the Hittorf method. C and A are the cathode and anode respectively; I_{M^+} and I_{A^-} are the cation and anion currents; S_1 and S_2 are arbitrary cross-sections defining the middle compartment of the cell; V_c and V_a are the cathodic and anodic compartments.

D the diffusion coefficient, and S the cross-sectional area of the cell.

The conditions are usually chosen so that the concentration of the solution in the middle compartment of the cell (V_m) does not change during the time (t) of the experiment. In this case the diffusional term $DS(\partial c/\partial x)$ vanishes, and

$$I_{M+} = \frac{IT_{M+}}{F}. \quad (8)$$

The overall cation balance in the compartment V_c is

$$\Delta P_{M+} = \frac{It}{F}(1 - T_{M+}) = \frac{It}{F} T_{A-}. \quad (9)$$

The quantity of anions moving out of V_c in time t is

$$\Delta P_{A-} = \frac{It}{F} T_{A-}. \quad (10)$$

The total change in the amount of the salt present in the cathodic compartment is

$$\Delta P_{MA} = \frac{It}{F} T_{A-} \quad \text{(equiv.)} \quad (11)$$

The same considerations can be applied to the anodic compartment. The values of ΔP_{MA} are obtained from the differences in concentration of the experimental solution before and after the experiment. The concentration differences produced by the passage of current are expressed in terms of the weight of solvent present in the solution at the end of the experiment. This allows for density changes, and therefore also volume changes, caused by changes in the amount of electrolyte.

The concentrations are usually found analytically by weighing the portion of the solution adjacent to the electrode. This method is therefore often referred to as the analytical or gravimetric method. Zhitomirskii and coworkers[286] have used a tracer method of analysis.

Many different types of measuring apparatus have been described. All of them have a cathodic, an anodic, and a central (intermediate) compartment[26-33]. In some designs porous diaphragms are used, including diaphragms made of ion-exchange resins[27,34-37]. However, different values of the transport numbers are usually obtained with diaphragms.

The application of Hittorf's method is limited by a number of factors:

(a) The need to choose reversible electrodes, or to make allowance for secondary electrode processes[27,38]. In the absence of an exact knowledge of the secondary products of the reaction, the results may be seriously in error[39].

(b) Analytical precision of a high order is needed[27,30,33].

(c) The thermal operating regime of the measuring apparatus must be optimised[38,40-44].

Most experimenters have confined their measurements to relatively small concentration changes: increasing the duration of electrolysis or the current enhances the effect of mixing (whether diffusional or convectional) on the results.

The accuracy of the results is also significantly influenced by the electrolyte concentration, since the relative concentration changes decrease, other things being equal, with increase in the concentration of the solutions. With dilute solutions different workers[38,45] have obtained results agreeing to 0.2% using Hittorf's method. However, the achievement of high precision presents real difficulties, and the moving boundary method is now used instead for accurate measurements of transport numbers.

III. METHODS BASED ON MEASUREMENTS OF THE E. M. F. OF GALVANIC CELLS

Measurements of the electromotive force (e.m.f.) of galvanic cells form the basis of two methods for measuring transport numbers. The first of these (the e.m.f. method) makes use of electromotive force measurements on concentration cells[46-49]. In the second method one measures the electromotive force of galvanic cells subjected to an external gravitational field[50-60].

The processes occurring in galvanic cells can be classified as thermodynamically reversible processes, and therefore thermodynamic methods are used to study them[61,62].

The electrical work done by a cell, excluding the mechanical work associated with any volume change, is equal to the change in the free energy G attending the process in the cell. At constant temperature and pressure dG can be expressed in terms of the change in the chemical potential μ_i of the individual components:

$$dG = Fde = \sum_i d\mu_i. \quad (12)$$

The quantity μ_i can itself be written in the form

$$\mu_i = \mu_i^0 + RT \ln a_i, \quad (13)$$

where μ_i^0 is the chemical potential in the standard state, R is the gas constant, T the temperature, and a_i the activity of the i-th component. These considerations are applied in calculating the e.m.f. of cells.

Concentration cells are a particular type of galvanic cell. Unlike the cells used as a source of e.m.f., whose electrical energy is derived from an overall chemical reaction, concentration cells derive their electrical energy from the tendency of the concentrations in different parts of the cell to reach a common level. According to the nature of the processes accompanying the equilibration of concentration, concentration cells can be divided into two types.

(a) Concentration cells without transport, of the type $\ominus$ reversible A electrode | $MA(c_1)$ | reversible M electrode $MA(c_2)$ | reversible A electrode $\oplus$. In such a cell there is no direct transport of electrolyte from one solution to the other. The solutions are separated by an additional reversible electrode. Transport takes place indirectly, as a result of chemical reactions. If the activities of the solutions differ by an amount da, the electromotive force of a cell without transport can be expressed, in general, by

$$de = \pm \frac{\nu}{\nu_\pm} \cdot \frac{RT}{z_\pm F} d \ln a, \quad (14)$$

where ν is the total number of ions formed when a solute molecule dissociates, and $\nu_\pm$ and $z_\pm$ are the number and the electrovalence, respectively, of ions of one sign. The $\pm$ signs refer to the ions with respect to which the external electrodes are reversible.

(b) Concentration cells with transport, of the type $\ominus$ reversible A electrode | $MA(c_1)$ | $MA(c_2)$ | reversible A

electrode ⊕ , have a liquid boundary between the solutions of different concentration. A diffusion potential, determined by the mobility difference between cations and anions, arises at the liquid junction. The value of the diffusion potential depends on the difference between the work needed to transfer anions from the more concentrated to the more dilute solution and the work needed to transfer cations from the more dilute to the more concentrated solution. The e.m.f. of a concentration cell with transport (ϵ_t) can be expressed as

$$d\epsilon_+ = \pm T_\pm \cdot \frac{\nu}{\nu_\pm} \cdot \frac{RT}{z_\pm F} d\ln a, \qquad (15)$$

where $T_\pm$ is the transport number of the ion with respect to which the electrodes are irreversible. Eqns. (14) and (15) are used in the e.m.f. method.

Two modifications of the e.m.f. method are used to measure transport numbers. In one of these electromotive forces are measured in cells with and without transport containing the same electrolyte. The concentration of one of the solutions is kept constant, whilst the concentration of the other is varied. Transport numbers are obtained from the slope of plots of $\epsilon = f(\ln a)$, according to the expression

$$\frac{d\epsilon_+/d\ln a}{d\epsilon/d\ln a} = T_\pm, \qquad (16)$$

where a is the activity of the solution whose concentration is varied.

The activities of the solutions of different concentrations should be determined independently. The activity is sometimes calculated from the concentration of the solution [$a = f(c)$] by means of the extended Debye–Hückel formula[63].

In the second modification of the e.m.f. method one measures the electromotive force of two concentration cells with transport, in one of which the diffusion potential is reduced to a minimum by introducing an intermediate electrolyte in which the cations and the anions have very similar mobilities[47,48,64]. Solutions of KCl or NH_4NO_3, which have been fully characterised, are commonly used as the intermediate electrolyte.

Many designs of cell have been used for the measurement of transport numbers[47,48,65–68]. A great deal of attention has been paid to the choice of electrodes[69–78] and to the formation of the liquid junction[79–84]. The use of this method is often limited by the difficulty of setting up satisfactory concentration cells. The need to establish the relation $a = f(c)$ complicates the procedure and introduces further errors.

The earliest report of the appearance of an electromotive force in a galvanic cell under the influence of external forces is due to Collie[50,51]. A thermodynamic discussion of the effect can be found in many monographs[2,3,8,52,57–61]. The essential features of the measurement are shown in Fig. 2. Vessel *1*, containing the reversible electrodes *2* and *3*, is filled with a solution of the experimental electrolyte MA and is subjected to the field of gravitational forces f. The cations and the anions, having different masses m_i and volumes V_i, move with different speeds in the gravitational field. The faster ions charge the electrode *3* to a potential ϵ. The charge on the electrode in equivalent to a definite internal electric field $E = \epsilon/h$, whose effect is to equalise the velocities of the ions. Allowing for the repulsive forces which act on the ions in

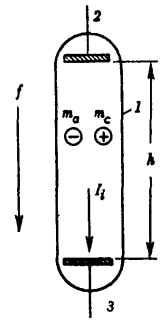

Fig. 2. Measurement of the electromotive force of a galvanic cell in a gravitational force field: 1) solution; 2) and 3) electrodes; h — interelectrode distance; f — external force; I_i — flux of the ith component; m_c and m_a — masses of the cation and anion.

the solution, the expression for the fluxes of cations and anions takes the form

$$I = c_i(u_i m_i g - u_i V_i \rho g \pm u_i \frac{\epsilon F}{h}), \qquad (17)$$

where c_i is the concentration of ions of the i-th kind, ρ the density of the solution, and g the acceleration due to the gravitational force.

The + sign corresponds to the slow ion, the - sign to the fast ion. In the gravitational field the movement of the ions causes transport of the solute as a whole, and the cell becomes a concentration cell. In time, the e.m.f. of the concentration cell opposes its gravitational electromotive force. Time changes of the e.m.f. have been observed experimentally[85,87]. The resulting e.m.f. can be calculated by imposing the condition of equal cation and anion fluxes:

$$\epsilon = -\frac{gh}{F}[T_c(m_c - V_c\rho) - T_a(m_a - V_a\rho)] + \epsilon_1,$$

where

$$\epsilon_1 = (T_a - T_c + 1)\frac{RT}{F}\ln\frac{\gamma_2\left[c_1 + \int_0^t AI_i(t)\,dt\right]}{\gamma_1 c_1},$$

c_1 is the initial concentration, $\gamma_{1,2}$ are the activity coefficients, and A is a parameter describing the distribution of the solution in the cell.

In the particular case of systems consiting of iodide solutions (such as KI with a small amount of free iodine) the transport number is calculated by the formula

$$T_{K^+} = \frac{\epsilon F\left|gh + \frac{1}{2}(M_{I_2} - V_{I_2}\rho)\right|}{M_{KI} - \overline{V}_{KI}\rho}, \qquad (19)$$

where M_{KI} and $\overline{V}_{KI}$ are the molecular weight and the partial volume of the salt and M_{I_2} and V_{I_2} the molecular weight and partial volume of the free iodine.

A considerable enhancement of the effect has been achieved by placing the galvanic cell in a centrifuge[55,56,85,86]. An e.m.f. generated by the centrifugal acceleration arises at the electrodes of the cell, located at distances r_1 and r_2

from the centre of rotation. To calculate the transport numbers, one uses formula (19) with the substitution

$$gh = 2\pi^2 n^2 (r_2^2 - r_1^2), \qquad (20)$$

where n is the number of revolutions per second.

As in the e.m.f. method, reversibility of the electrodes is an essential requirement in measurements of transport numbers by the gravitational method. Radial temperature gradients must also be carefully avoided[58].

Measurements of transport numbers by the e.m.f. method and by the method based on e.m.f. measurements on a galvanic cell in a gravitational force field are inferior in accuracy to measurements by the moving boundary method. In all these methods serious difficulties arise in the treatment of results for multicomponent systems: these require a knowledge of the relationship between the e.m.f.'s of the galvanic cells and the transport numbers of the individual components[68,88-90].

IV. METHODS BASED ON OBSERVATIONS OF IONIC BOUNDARIES

1. General Considerations and Stability Conditions of Ionic Boundaries

The existence of stable ionic boundaries between electrolytes[5,6,91] has been used as the basis for several methods of measuring transport numbers. The conditions under which such boundaries can exist, and their main features, arise from the following considerations. An ionic boundary can be formed between two electrolytes M_1A and M_2A whenever the mobilities of the non-common ions ($u_{M_1^+}$ and $u_{M_2^+}$) differ by a sufficient amount. To this end, the electrolytes are positioned so that $u_{M_1^+}$ and $u_{M_2^+}$ increase in the direction in which the ions move in the electric field (Fig. 3). The passage of an electric current through the electrolytes generates a stable boundary between the electrolytes, arising from the difference in mobility between the cations. When the electrolytes on either side of the boundary have reached a steady state, i.e. when their concentrations cease to change, the velocities v_1 and v_2 of the ions M_1^+ and M_2^+ become identical and equal to the velocity of the boundary (v_b):

$$v_1 = v_2 = v_b. \qquad (21)$$

If the solution as a whole does not move, we have

$$v_b = u_{M_1^+} \cdot E_1 = u_{M_2^+} \cdot E_2, \qquad (22)$$

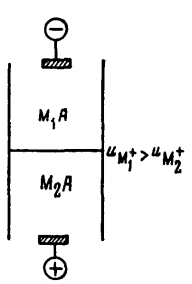

Fig. 3. Measurements by the moving boundary method.

where E_1 and E_2 are the electric field strengths in the electrolytes M_1A and M_2A respectively. Expressing E in terms of the current density j, we can write

$$v_b = jT_{M_1^+}/Fc_1 = jT_{M_2^+}/Fc_2, \qquad (23)$$

for the velocity of the boundary, where $T_{M_1^+}$ and $T_{M_2^+}$ are the transport numbers of the cations and c_1 and c_2 the concentrations of the solutions M_1A and M_2A.

The relation known as Kohlrausch's "regulating function"[92] follows from condition (23). Since in a steady state the fluxes of solvent on either side of the boundary must be equal[93], the regulating function can be written in the form

$$\frac{T_i}{c_i'} = \text{const.}, \qquad (24)$$

where c_i' is the electrolyte concentration expressed in equiv. per kg of solvent.

If the concentration of the indicator electrolyte (the solution containing the slower M^+ ions) does not satisfy relation (24), a concentration readjustment takes place as electrolysis proceeds[4,94]. The concentration change during this readjustment[95-97] is described by the following differential equation:

$$-\frac{\partial c}{\partial t} = \frac{j}{F} \cdot \frac{\partial T(c)}{\partial c} \cdot \frac{\partial c}{\partial x} - D\frac{\partial^2 c}{\partial x^2}. \qquad (25)$$

Ignoring the diffusional term, we can write an expression for the rate of readjustment[94], i.e. for the velocity of the Kohlrausch concentration front relative to that of the boundary:

$$v_{readj} = v_b - \frac{j}{F}\frac{\Delta T(c)}{\Delta c}. \qquad (26)$$

In most solutions the change in transport number with concentration, $\Delta T(c)/\Delta c$, is not large, and to a first approximation the Kohlrausch concentration front moves away from the boundary with the speed of the ions. The time needed to establish a steady state is

$$\tau = \frac{l}{v_{readj}}, \qquad (27)$$

where l is the length of the region over which the concentrations adopt the Kohlrausch value.

For univalent ions, the concentration ratio of the solutions in the region of the boundary can be obtained from the relation

$$\frac{c_2}{c_1} = b \cdot e^{-\frac{u_1 - u_2}{u_1} \cdot \frac{e}{kT} \cdot \frac{v_b x}{u_2}}, \qquad (28)$$

where b is a constant, u_1 and u_2 are the mobilities of the non-common ions, k is Boltzmann's constant, T the absolute temperature, e the electronic charge, and x the distance measured from the origin of the system of coordinates.

This expression can be used to calculate the width of ionic boundaries.

The stability of the boundary and the rate of readjustment depend essentially on a correct choice of the operating conditions of the measuring tube, in particular the range of currents and electric fields. The evolution of Joule heat causes various effects, which can seriously affect methods based on ionic boundaries. The following are the most significant effects associated with the temperature conditions:

(a) Change in temperature of the solution. Due to the evolution of Joule heat, the motion of the boundary occurs at a temperature which is not the same as that of the surroundings. The change of transport with temperature will cause a change in the Kohlrausch concentration.

(b) Ionic convection. Since the mobility of the ions is a function of temperature, ions at different distances from the centre of the tube will have different velocities:

$$v_i = [u_0 + \beta\Delta T(\rho)]E, \qquad (29)$$

where β is the temperature coefficient of mobility and u_0 the mobility of the ions at temperature T_0.

Since the boundary moves at an average velocity v_b, the speed of the ions in some central region will exceed that of the boundary, whilst the speed of the ions close to the walls wil be somewhat less than the speed of the boundary. Thus, ionic convection will occur along the tube with a velocity $\Delta v_i = v_i - \bar{v}_b$. This motion of the ions is equivalent to an additional contribution to diffusional mixing[99-101]. The increase in the effective diffusion coefficient causes the boundary between the electrolytes to become diffuse.

(c) Convective entrainment of indicator electrolyte. This phenomenon occurs because some of the indicator electrolyte is carried into the overlying electrolyte by convective flow. Usually, the boundary remains fairly sharp, but the velocity of the boundary becomes a non-linear function of the current[101]. Convective entrainment of the indicator electrolyte is associated with the difference in temperature between the top solution and the indicator solution, and can be minimised by suitable choice of the thermal regime under which the tube is operated. Alternatively, the measuring tube can be packed with a porous filler[102].

Several procedures for forming the boundaries and observing their position are known. A sharp separation between solutions can be obtained by the following methods.

(a) The sheared boundary method[103]. The simplest form of this method is illustrated in Fig. 4*a*. Two carefully lapped plates *1* and *2* are provided with openings in which are located the tips of tubes *3* and *4*, filled with different solutions. By sliding the plates, the tips of the tubes are brought into contact, and the drops of solution protruding from the tips are sheared together and generate a sharp boundary.

(b) The air bubble (air lock) method[104]. Fig. 4*b* shows part of the measuring tube. Vessels *5* and *6* are initially filled with a solution of the top electrolyte; an air bubble which separates the solution into two parts is introduced into the capillary *8* through the side tube *7*. Vesel *6* is then filled with a solution of the indicator electrolyte. A sharp boundary is obtained when the air bubble is forced out of capillary *8* into tube *7*.

(c) The self-generated boundary method[105]. The method (Fig. 4*c*) makes use of a soluble electrode *9*, above which is located the solution of M_1A. The solution of indicator electrolyte M_2A is formed by electrolysis, and is separated from the top electrolyte by a sharp boundary. Cady and Longsworth have pointed out[106] that the automatic adjustment of the concentration of the indicator electrolyte is confined to the immediate vicinity of the boundary.

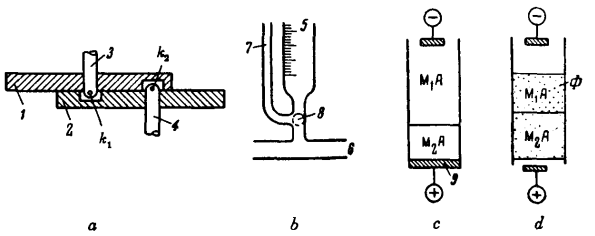

Fig. 4. Methods of forming ionic boundaries: *a*) sheared boundary method; *b*) air bubble method; *c*) self-generated boundary method; *d*) porous packing method; 1) and 2) lapped plates; 3), 4), 5), and 6) parts of the measuring tube; 7) and 8) capillaries; 9) a soluble electrode; k_1 and k_2 — drops of the solutions; Φ — the porous packing.

(d) The porous packing method[102,107]. The solutions of M_1A and M_2A are joined in the porous filter Φ (Fig. 4*d*). A boundary forms automatically when the current is switched on. The porous packing minimises mixing effects and eliminates convection of the solutions.

Various methods are used to observe the boundaries. The most important of these are as follows.

(a) Optical methods. Visual observation is used when one of the solutions contains coloured ions or when the refractive indices of the two solutions are very different. Occasionally, penumbra projections are photographed[44,95], or one observed the diffraction pattern produced on a screen behind the measuring tube by a narrow beam of light[98].

(b) Methods based on conductivity and temperature differences between the top and the indicator electrolyte. The position of the boundary is monitored either by auxiliary electrodes[35,108-112,287,288] or by miniature thermistors[113] located inside the tube.

(c) Methods involving radioactive tracers[107,114,115,289]. Small amounts of β- or γ-active isotopes of the same elements are added to one or both of the experimental solutions. The position of the boundary is detected by accurately collimated radiation counters.

The methods of measuring transport numbers which rely on ionic boundaries can be divided into two groups: the direct methods, including the moving boundary method and the method of simultaneous observation of the motion of the ions and of the solution, and the indirect methods, based on the use of Kohlrausch's regulating function.

2. The Moving Boundary Method

Expression (23), relating the transport number to the velocity of the boundary, forms the basis of the moving boundary method. The displacement of the boundary caused by the passage of a known quantity of electricity is measured experimentally[91,106,116,117]. A vertical cross-section through part of the measuring tube is shown in

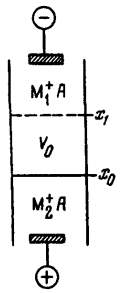

Fig. 5. Measurements by the moving boundary method: x_0 — initial position of the boundary; x_1 — final position of the boundary.

Fig. 5. The volume V_0, defined by the cross-sections with coordinates x_0 and x_1, is usually identified by fiducial marks and accurately measured before the experiment. By measuring the time t needed for the boundary to move between the marks, and knowing the current I and the concentration C_{M^+} of the electrolyte under study, the transport number can be calculated:

$$T_{M^+} = \frac{V_0 C_{M^+} F}{It}. \qquad (30)$$

Various corrections are usually applied to the formula. Miller[94] first drew attention to the fact that the volume change due to electrolysis and ion migration induces a drift of the solution relative to the measuring tube. An appropriate correction to the volume V_0 can either be determined experimentally[8,61,118-133] or calculated from data on the density of the solutions and of the electrode components[134]. At low concentrations of the experimental solutions another correction becomes necessary: it arises from the transport of current by the ions formed by dissociation of the solvent and of trace impurities[135]. Allowing for these effects, the expression for calculating the transport number takes the form

$$T_i = \frac{F}{It} c_i (V_0 - \Delta V) \frac{1}{1 - \frac{L_0}{L}}. \qquad (31)$$

where ΔV is Miller's correction, L the electrical conductivity of the solution, and L_0 the electrical conductivity arising from impurities.

Measurements by the moving boundary method are complicated by the need to choose the concentration of the indicator electrolyte, c_{ind}, in preliminary experiments. The velocities of the ions are equal to the velocity of the boundary if the state of the electrolytes is stationary ($\partial c/\partial t = \partial c_{ind}/\partial t = 0$), i.e. if Kohlrausch's regulating function is obeyed. It has been shown[106,109] that Kohlrausch conditions are established automatically and exactly only if the initial concentration of the indicator electrolyte, c_{ind}^{init}, is not very different from the Kohlrausch value c_{ind}^{K}. In practice, the difference between the two values should not be more than 5–10%. At larger deviations, the rearrangement process gives rise to an additional mode of transport of the solution as a whole. Since the value of c_{ind}^{K} is not known before the experiment, the normal procedure is to determine the relationship $T_i = f(c_{ind}^{init})$, whose form is shown in Fig. 6. The value of c_{ind}^{K} is taken

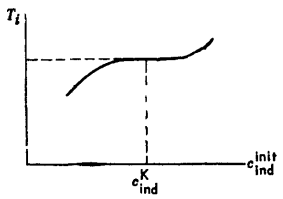

Fig. 6. Variation of the transport number with concentration of the indicator electrolyte during measurements by the moving boundary method.

to be the mid-point of the range over which the transport number remains constant.

The precision of transport number measurements decreases with increased concentration of the experimental electrolytes, because the correction for the transport of solution as a result of the motion of the boundary becomes larger.

The maximum concentration of the solutions which can be studied by the moving boundary method is no more than 0.1 N. The limitation arises from convective transport and convective entrainment effects. The use of a porous filler is not permissible, because the effect of electro-osmotic solution transport cannot be allowed for when using this method.

The analytical and the differential moving boundary methods are variants of this procedure.

The principle of the analytical method is as follows. The measuring tube, divided into two compartments by the porous diaphragm Φ (Fig. 7), is filled with the electrolytes M_1A and M_2A. When current is passed, the boundary emerges from the filter (position x_0) and reaches position x_1 after time t. The amount of M_2^+ ions above the filter is determined by a conventional analytical procedure, and hence the transport numbers in a solution of M_2A can be obtained. The calculation is based on a formula analogous to Eqn. (30):

$$T_{M_2^+} = \frac{V_0 C_{M_2^+} F}{It}. \qquad (32)$$

The shortcoming of this method is the uncertainty as to the concentration of the M_2A solution, which penetrates

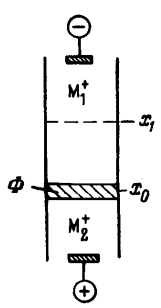

Fig. 7. Analytical form of the moving boundary method: Φ — porous diaphragm; x_0 and x_1 — initial and final positions of the ionic boundary.

into the volume above the filter if the initial concentrations of the leading solutions are not chosen in accordance with the Kohlrausch regulating function. In general, this should lead to a dependence of the results upon the concentration of the leading electrolyte.

The differential method[117] makes use of concentration boundaries[92,94,137,138], i.e. the boundaries formed by solutions of different concentrations c' and c'' of the same salt. The volume swept by the boundary is proportional to the difference in transport number of the ions at concentration c' and c''. Generally, the method is used to measure the concentration dependence of transport numbers, and is useful also when the direct method cannot be used[139]. The formula in this case is:

$$T'_{M+} - T''_{M+} = \frac{V_0 (c' - c'') F}{It}. \qquad (33)$$

The main limitation of this method is associated with the stability of concentration boundaries[96].

The precision of measurements by the moving boundary method depends essentially on the accuracy with which the ionic boundaries can be located. According to Spiro's review[2], the maximum attainable precision of the method is 0.03%.

3. Simultaneous Observation of the Motion of the Ions and of the Solution

Kaimakov and Fiks[102] have developed a method of measuring transport numbers which is free from the limitations and shortcomings inherent in the moving boundary method. Whereas in the moving boundary method the system of coordinates is based on the measuring tube, and allowance for the transport of solution has to be made by applying the Miller correction, in the method of simultaneous observation one measures the flow of solvent passing through the ionic boundary by observing the motion of the ions and of the solution at the same time. In general, transport of the solution can be caused by: (a) a difference in levels of the liquids in the cathodic and the anodic limb of the measuring tube (countercurrent); (b) a difference in density between the leading and the indicator solution; (c) electrode processes, and displacement of the boundaries; (d) electro-osmotic flow of the solution.

If the solution undergoes transport under the influence of external forces, the velocity of the boundary v_b is the sum of the velocities v_i of the ions and v_s of the solution:

$$v_b = v_i + v_s, \qquad (34)$$

or

$$v_i = v_b - v_s = \frac{fT_i}{Fc}.$$

This is the basic formula of the method of simultaneous observation of the motion of the ions and of the solution.

The essential features of the measurement of transport numbers are illustrated in Fig. 8. The measurements are made in a U-tube in which a porous plug *3* separates the cathodic limb *1* from the anodic limb *2*. The plug acts as a hydrodynamic resistance, and also as the region where the boundary is formed. The measurement of transport numbers consists, essentially, in measuring the velocity of the boundary and that of the solution over a range of current densities, and plotting $v_b = f(I)$ and $v_s = f(I)$. Clearly, the difference between the two curves

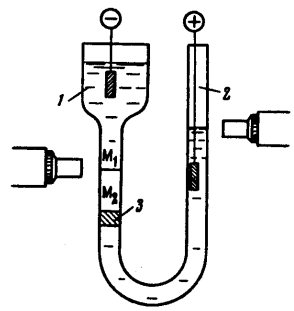

Fig. 8. Measurements by the method of simultaneous observation:
1) cathodic limb of the measuring tube;
2) anodic limb of the measuring tube;
3) porous diaphragm.

must be a straight line whose slope is related to the transport number by the expression

$$\tan\alpha = \frac{T_i}{Fc_i}, \qquad (35)$$

where c_i is the concentration of the ions in equiv. litre^{-1}.

The form of the experimental plots is shown in Fig. 9.

In the method of simultaneous observation there is no need to make a correct choice of the concentration of the indicator electrolyte. The perturbation of the hydrodynamic equilibrium associated with the establishment of the Kohlrausch concentration is automatically allowed for. The use of a countercurrent to control the motion of the boundary, in conjunction with a porous septum, makes a much wider range of temperatures and electrolyte concentrations experimentally accessible.

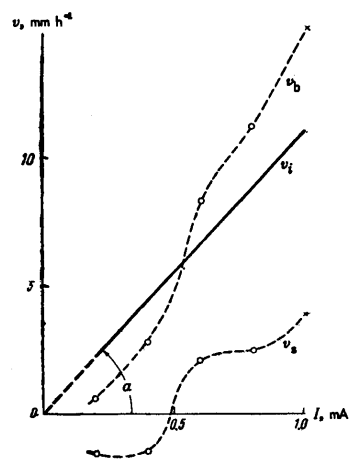

Fig. 9. Experimental curves obtained by the method of simultaneous observation[102] for 3 *N* solutions of NH_4Cl at 20°:
v_b — velocity of the ionic boundary; v_s — velocity of the solution; v_i — velocity of the ions.

The most important measurements, in practice, are made by keeping the boundary immobile with a suitable countercurrent, and measuring the accumulation of solvent in the anodic limb[101]. The transport number of the cations is calculated by means of the formula

$$T_{M+} = \frac{F}{I} v_s \cdot c_i' S_A, \qquad (36)$$

where v_s is the rate of accumulation of solvent in the anodic limb, c_i' the concentration of the ions in equiv. per kg of solvent, I the total current through the cell, and S_A the internal cross-sectional area of the anodic limb.

Thus, the cross-section of the tube which contains the boundary does not appear in the formula. When calculating transport numbers allowance should be made for possible changes in the volume of the solvent being accumulated[101,140].

The method of simultaneous observation has provided many data relating to concentrated solutions of electrolytes. In principle, this method should give results no less accurate than those of the moving boundary method.

4. Methods Based on Kohlrausch's Regulating Function

In the direct methods transport numbers can be deduced immediately from the results of a single experiment. The methods relying on the regulating function enable transport numbers to be calculated from a knowledge of the steady-state concentrations of the electrolytes moving in constant relative positions, and of the transport number of one of them. The problem of measuring transport numbers consists essentially in making the correct choice of electrolytes and experimentally determining their steady-state concentrations. Cady and Longsworth[106] were the first to measure steady-state concentrations. Hartley[93] proposed a method of measuring steady-state concentrations which he later used in a number of investigations[141-145]. Conductimetric analysis has also been used to measure concentrations[109,146]. Fig. 10 shows part of the measuring tube of Samis and Hartley's apparatus[147]. The leading electrolyte solution, in tube *1* and vessel *2*, was brought into contact with the indicator electrolyte in tube *4* by the air-lock method, using the side-arm *3*. When current was passed the boundary moved along tube *1*. By partial compensation of the motion of the boundary, using a countercurrent, some solution having the Kohlrausch concentration was forced into vessel *5*, provided with measuring electrodes.

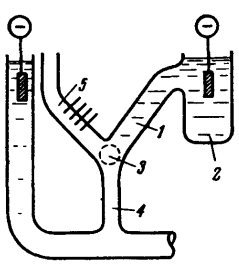

Fig. 10. Part of Samis and Hartley's apparatus[147] for measuring Kohlrausch concentrations:
1) leading electrolyte solution; 2) cathode vessel; 3) capillary connection; 4) indicator electrolyte; 5) auxiliary vessel with leads for measuring the electrical conductance of the electrolytes under study.

The upper limit of experimentally accessible concentrations, 0.1 N, was set by the fact that no precautions were taken to minimise the effect of convective transport.

Refractive analysis has also been used[44,95,148,149] to measure steady-state concentrations.

Some new procedures were developed when the problems associated with readjustment in concentrated solutions were overcome. Work with concentrated solutions is characterised by the need to avoid convective transport effects. This is achieved either by working with small-diameter tubes, or by using porous packing. Konstantinov and Oshurkova[98] made their measurements in capillaries of ~0.1 mm diameter, using large electric fields. Steady-state concentrations were determined by measuring the length of a thread of the experimental solution, "trapped" between the leading and the indicator solution.

Kaimakov and coworkers[150-152] used wide measuring tubes packed with ground quartz. Steady-state concentrations were measured either with platinum electrodes fitted to the tubes or with a miniature thermistor. By this procedure, steady-state concentrations could be measured in a single experiment for a number of electrolytes following each other.

V. MEASUREMENT OF TRANSPORT NUMBERS AND MOBILITIES IN MIXTURES OF ELECTROLYTES

Both the Hittorf method[151-161] and the moving boundary method[117,162-166] have been used to study mixtures of electrolyte solutions. To measure transport numbers by Hittorf's method, the concentration changes of all the components of the solution in the electrode compartments are measured simultaneously by chemical analysis. The lower limit of additive concentration is set only by the precision of the method of chemical analysis of the particular component. The upper limit of the total concentration of the mixture is set by convective mixing[167]. The early investigations of mixtures by Hittorf's method[154,155,292] relied on inadequate methods of analysis, and led the authors to erroneous conclusions as to the structure of mixtures of binary electrolytes. The most accurate results are obtained by the moving boundary method. A boundary is formed between the mixture and the indicator electrolyte, and an electric field is applied which causes the mixture to separate and form a second boundary between ions of different mobility. The velocity of this boundary is proportional to the transport number of the ion of the additive[117]. The use of the moving boundary method is confined to relatively low total concentrations of the mixture under study ($c_{tot} < 0.1$ N). A procedure for measuring the mobilities and transport numbers of ions added at low concentrations (a few per cent, or fractions of one per cent) to concentrated solutions of electrolytes has been described[168-170]. The method depends on separating the mixture in an electric field, the impurity ions accumulating between the mixture and the indicator electrolyte. The boundaries are located within the porous packing. The column of additive is held in a fixed position relative to the measuring tube by a counterflow. The transport number of the additive is found

TABLE 1. Transport numbers of cations in aqueous electrolyte solutions.

Compound	t°C	Electrolyte concentration, N																	Method	Literature references
		0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	1.5	2.0	3.0	5.0	6.0	7.0	9.0	10.0	12.0	15.0	
$AgClO_3$	25			0.499																m.b.	176
$AgClO_4$	25	0.4783	0.4781	0.4774	0.4774															m.b.	177,176
$AgNO_3$	18		0.471	0.471	0.472	0.472	0.473	0.481	0.499	0.513	0.524									Hitt.	176, 19—25,40,120, 162,172,178—186, 188,190,191,282
	25	0.4647	0.4648	0.4652	0.4664															m.b.	177,136
	40			0.4729	0.4737															m.b.	191
$AgNO_3$	25	0.481	0.461																	Hitt.	192
Ag_2SO_4	17				0.446															Hitt.	19—25
Ag_2SiF_6	22			0.475																Hitt.	176
$BaCl_2$	18		0.450	0.450	0.440	0.420	0.408	0.389	0.360	0.350	0.343									Hitt.	172,36,178,180,181,
	25			0.439	0.426	0.418	0.406	0.386	0.377	0.374	0.372									e.m.f.	193—197,49, 52—54
$BaBr_2$	18	0.436	0.441		0.420	0.410														Hitt.	198
BaI_2	18			0.426		0.415														m.b.	197
$Ba(NO_3)_2$	25				0.456	0.456	0.455	0.446												Hitt.	198
$CaBr_2$	18			0.409		0.396														m.b.	172,197,199
$CaCl_2$	15	0.4261	0.4231	0.4188	0.4105	0.4024	0.3964	(0.15)												m.b.	200
	25			0.420	0.413	0.404	0.387	0.339	0.289	0.268	0.259	0.253	0.252	0.251						e.m.f.	49,120,200,201
	35	0.4354	0.4424	0.4281	0.4198	0.4117	0.4057	(0.15)												m.b.	200
CaI_2	18			0.416	0.400															m.b.	202
$Ca(NO_3)_2$	20	0.450																		Hitt.	202,203
$Ca(OH)_2$	25	0.214																		Hitt.	178,180,181
$CaSO_4$	18	0.441																		m.b.	202,203
$CdBr_2$	25			0.434	0.431	0.426	0.408	0.358	0.222	0.152	0.078	0.028	—0.166							e.m.f.	204,178,180,181,194, 196,205
$CdCl_2$	25			0.486	0.463	0.460	0.471	0.499	0.471	0.424	0.381	0.307	0.161	0.095	0.037	—0.105	—0.192			e.m.f.	204,178,180,181,194, 196,205
$CdCl_3$	20					0.4338														m.b.	206
CdI_2	18	0.445	0.442	0.440	0.440	0.317	0.160	0	—0.12	0.18	0.22									Hitt.	172
$CdSO_4$	18		0.388	0.384	0.378	0.369	0.349	0.323	0.294		0.254									Hitt.	194,196,202,203
	25	0.384	0.384	0.384	0.384	0.384	0.369	0.328	0.295	0.279	0.265	0.240	0.195							e.m.f.	204,207,208
$CeCl_3$	25		0.4636	0.4582	0.4494	0.4390														Hitt.	45,87
$CoBr_2$	18		0.397	0.397	0.390															Hitt.	172,209
$CoCl_2$	20					0.346	0.339	0.321	0.299	0.281	0.266	0.247	0.224	0.215	0.209					s.o.	151,178,180,181,210
$Co(NH_3)_6Cl_3$	25		0.5673		0.5647															m.b.	210
CsBr	18			0.497		0.493														m.b.	197
CsCl	25			0.390	0.377	0.365	0.346	0.336												Hitt.	211,178,180,181,197
CsI	18			0.497		0.497														m.b.	197,86,212
$CuBr_2$	25						0.445	0.440	0.420	0.325	0.285	0.138	0.037	0.09	—0.146					Hitt.	209
	35							0.365	0.275	0.165	0.133	0.042	—0.145	—0.238	—0.335					Hitt.	213
$CuCl_2$	20							0.351	0.331	0.315	0.301	0.278	0.251	0.245	0.240	0.233				s.o.	39,178,180,181,198, 209,213
$CuSO_4$	18			0.375	0.375	0.375	0.357	0.328	0.304	0.286	0.280									Hitt.	172, 19—25,178,180, 181,193,194,196, 198,214,215
	25					0.359	0.339	0.304												m.b.	216
$ErBr_3$	25			0.4366	0.4248	0.4121														m.b.	217
$ErCl_3$	25		0.4489	0.4429	0.4338	0.4230														m.b.	45
$EuCl_3$	25		0.4595	0.4564	0.4472	0.4357														m.b.	45,206
$GdBr_3$	25		0.4552	0.4501	0.4380	0.4271														m.b.	217
$GdCl_3$	25		0.4603	0.4548	0.4409	0.4314														m.b.	217,206
HBr	25					0.729														Hitt.	218
HCl	5	0.844	0.845	0.846	0.848	0.850	0.851	0.854	0.855	0.857	0.857	0.858								e.m.f.	219,26,135,162,178, 180,181
	10	0.840	0.841	0.842	0.844	0.846	0.847	0.850	0.852	0.853	0.853	0.854									190,191,193,194,196, 220—229
	15	0.834	0.835	0.836	0.838	0.840	0.843	0.846	0.848	0.849	0.849	0.850								e.m.f.	219
	15								0.848	0.850	0.852	0.850	0.829	0.795	0.726	0.658	0.649	0.629		e.m.f.	290
	20	0.829	0.830	0.832	0.834	0.837	0.839	0.842	0.844	0.845	0.846	0.846								e.m.f.	219, 52—54
	20								0.845	0.846	0.851	0.853	0.822	0.795	0.759	0.661	0.599	0.466		s.o.	101
	25								0.841	0.843	0.844	0.843	0.824	0.791	0.717	0.665	0.647	0.633		e.m.f.	290,289
	30	0.819	0.821	0.822	0.825	0.828	0.830	0.834	0.837	0.839	0.839	0.840								e.m.f.	219
	35	0.814	0.816	0.818	0.821	0.823	0.827	0.831	0.833	0.835	0.835	0.836								e.m.f.	219
	35								0.834	0.835	0.836	0.835	0.816	0.786	0.710	0.654	0.645	0.632		e.m.f.	290
	40	0.809	0.811	0.813	0.816	0.819	0.823	0.827	0.829	0.830	0.831	0.832								e.m.f.	219
	45	0.804	0.806	0.808	0.811	0.814	0.818	0.822	0.824	0.825	0.826	0.827								e.m.f.	219
	50	0.799	0.801	0.803	0.806	0.810	0.814	0.819	0.821	0.822	0.822	0.823								e.m.f.	219

TABLE 1 (contd.)

Compound	T, °C	Electrolyte concentration, N																	Method	Literature references
		0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	1.5	2.0	3.0	5.0	6.0	7.0	9.0	10.0	12.0	15.0	
$HClO_4$	25			0.8462	0.8471	0.8453														m.b.	187
HI	25				0.825	0.828	0.825													Hitt.	189,55,56
HIO_3	25		0.9013	0.9034	0.9065	0.908														m.b.	128
HF	25			0.860	0.845	0.821	0.787	0.732	0.694	0.677	0.664									Hitt.	230
HNO_3	18	0.8336	0.8348	0.8360	0.8400	0.8437	0.8492													m.b.	231,194,196,222
H_3PO_4	25	0.959	0.958	0.956	0.953	0.946	0.938	0.927	0.919	0.914	0.909	0.904	0.898	0.896	0.891	0.891	0.889		(19.4)	e.m.f.	89,232
H_2SO_4	0					0.839	0.838	0.836	0.834	0.832	0.827	0.821	0.806	0.797	0.786	0.763	0.750	0.720	0.512	e.m.f.	
	10					0.834	0.834	0.831	0.828	0.826	0.821	0.819	0.797	0.787	0.776	0.754	0.741	0.708	0.508	e.m.f.	
	15					0.830	0.829	0.827	0.824	0.821	0.817	0.809	0.792	0.782	0.771	0.747	0.733	0.702	0.506	e.m.f.	210,178,180,181,
	25					0.819	0.819	0.818	0.817	0.815	0.807	0.799	0.781	0.770	0.759	0.736	0.722	0.691	0.502	e.m.f.	196, 233—236
	35					0.807	0.807	0.805	0.801	0.798	0.793	0.785	0.767	0.756	0.744	0.721	0.707	0.676	0.498	e.m.f.	
	45					0.793	1.793	0.791	0.787	0.784		0.769	0.751	0.741	0.729	0.707	0.693	0.663	0.494	e.m.f.	
	60					0.770	0.770	0.768	0.764			0.744	0.724	0.713	0.704	0.652	0.640	0.641	0.488	e.m.f.	
$HoBr_3$	25		0.4456	0.4385	0.4286	0.4169														m.b.	45
KBr	18		0.494	0.493	0.493	0.492	0.491	0.487	0.486	0.485	0.485	0.484								Hitt.	237,120,197,238
$KBrO_3$	18			0.567		0.570														m.b.	197
KCl	0	0.493	0.493	0.493	0.493	0.492	0.491													Hitt.	176,19—25,38,178, 180,181,
	10		0.495	0.495	0.495	0.495														Hitt.	135,190,196,197, 202,203,239
	15	0.4926	0.4925	0.4924	0.4923	0.4921														m.b.	240,26,36,104,111, 167,191, 240—248
	25		0.494	0.493	0.493	0.492	0.491	0.487	0.486	0.485	0.485	0.484								Hitt.	172,52—54
	25	0.4903	0.4902	0.4901	0.4900	0.4898		0.4887	0.4883											Hitt.	38,117,201, 249—251
	35	0.4887	0.4886	0.4885	0.4885	0.4888														m.b.	240
	45	0.4869	0.4868	0.4868	0.4869	0.4873														m.b.	240
$KClO_3$	18			0.534		0.536														m.b.	202, 19—25,197
$KClO_4$	25					0.570														m.b.	202,197
K_2CO_3	18				0.61	0.60	0.59	0.565	0.566	0.579	0.587	0.596	0.62							Hitt.	178,180,181
$K_3Fe(CN)_6$	25	0.485	0.515	0.555	0.604	0.647														m.b.	252,104
$K_4Fe(CN)_6$	25		0.4315		0.4384	0.4406														m.b.	252,104
KI	18		0.494	0.495	0.493	0.492	0.491	0.487	0.486	0.485	0.485	0.484								Hitt.	237, 19—25,54—58. 120,178,180,181, 197,212,253
$KMnO_4$	20	0.548	0.547	0.540	0.538	0.540	0.555	0.678	(0.4)											m.b.	254,178,180,181.
KNO_3	18					0.503	0.504	0.508	0.513	0.518	0.521									m.b.	172,19—25,162,197, 245
	25		0.5084	0.5087	0.5093	0.5103	0.5120													Hitt.	19—25,136,245
KOH	25			0.263	0.263	0.263	0.263	0.263	0.263											Hitt.	255
K_2SO_4	25	0.4818	0.4829	0.4848	0.4870	0.4890	0.4949													Hitt.	104,19—25, 194— —196,245,104,159,252
	35	0.494	0.488	0.489	0.483															Hitt.	197
$LaBr_3$	25					0.4574	0.4516	0.4426	0.4325											Hitt.	185
$LaCl_3$	25										0.4216	0.3935	0.3669	0.3459	0.3282	0.3012				Hitt.	257,36,45,256,258
LiCl	20																			s.o.	259,135,140,178,180, 181
	25			0.3296	0.3240	0.3192	0.3126	0.2994	0.2863	0.2765	0.2688	0.2571	0.265	0.244	0.224	0.218	0.217	0.216	0.214	0.210		Hitt.	110,48,52—55,167, 198,260,283,284
	40											0.264	0.242	0.240	0.238	0.236	0.235	0.234	(11.0)	s.o.	259,47,253,261
	60											0.277	0.260	0.257	0.255	0.255	0.256	0.257		s.o.	259
	90											0.300	0.276	0.278	0.279	0.283	0.286	0.289		s.o.	259
LiI	20		0.318																	Hitt.	262
	25						0.317		0.267											centr.	55,56,86,87,212
$LiNO_3$	20												0.312	0.323	0.334	0.358	0.376	0.412	0.420 (13.0)	s.o.	263
	30												0.307	0.318	0.330	0.359	0.375	0.408	0.425	s.o.	263
	40												0.313	0.322	0.334	0.360	0.378	0.411	0.422	s.o.	263
LiOH	18					0.150	0.150	0.140	0.13	0.11										Hitt.	198,172,262,97
Li_2SO_4	25			0.385	0.386	0.350			0.283	0.259	0.236	0.226	0.211							s.o.	264,262,97
$MgBr_2$	18																			m.b.	202
$MgCl_2$	18						0.320	0.308	0.291	0.280	0.271	0.250	0.224							Hitt.	202,172,178,180,181, 265
										0.292	0 277	0.253	0.226	0.217	0.212	0.209				s.o.	175,64,159,198
MgI_2	20			0.388		0.350														m.b.	202
$MgSO_4$	18		0.385	0.382	0.372	0.360	0.350	0.310	0.250	0.249	0.247	0.240								Hitt.	172,159,178,180,181

TABLE 1 (contd.)

Compound	t, °C	Electrolyte concentration, N																	Method	Literature references
		0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	1.5	2.0	3.0	5.0	6.0	7.0	9.0	10.0	12.0	15.0	
$MnBr_2$	18		0.490	0.490	0.486	0.470														Hitt.	172
$MnCl_2$	18		0.497	0.497	0.485	0.471														Hitt.	172
NaBr	18	0.395	0.395	0.395																Hitt.	178,180,181,172,198,202,19—26,48.52—54,
NaCl	18		0.396	0.395	0.392	0.389	0.380	0.377	0.363	0.360	0.358	0.354	0,350							Hitt.	120,135,176, 172
	25	0.3930	0.3918	0.3903	0.3878	0.3853															
	35	0.3970	0.3958	0.3944	0.3919	0.3822														m.b.	267 } 178,180
	45	0.4008	0.3996	0.3982	0.3957	0.3932														m.b.	267 } 181,198,202,237
Na_2CO_3	18				0.48	0.47	0.47	0.46	0.452	0.454	0.458									m.b.	267 } 244,266,97
NaI	18				0.381	0.376														Hitt.	198,172,178,180,181
	25						0.3827		0.384											m.b.	202,212
$NaHPO_3$	25		0.42		0.48	0.46														centr.	55,56,60
$NaNO_2$	19				0.371															Hitt.	269,268
NaOH	25		0.203	0.197	0.189	0.183	0.177	0.169	0.163											Hitt.	198,136,172,178,180, 181,285
																				e.m.f.	270,172,178,180,181, 198,202,271
$Na_3P_3O_{10}$	25		0.42		0.46	0.47														Hitt.	238
$Na_4P_2O_7$	25		0.42		0.48	0.54														Hitt.	258
$(NaPO_3)_n$	0				0.56	(0.041)														Hitt.	237
	25			0.56	(0.04)	0.54	(0.09)													Hitt.	253
Na_2SO_4	9						0.367	0.363	0.360	0.359										Hitt.	19—25
	25		0.3848	0.3836	0.3829	0.3828	0.3828													m.b.	120,178,180,181
NH_4Br	18			0.483		0.481														m.b.	19—25
NH_4Cl	25		0.4907	0.4906	0.4905	0.4907	0.4915													m.b.	172,19—25,120,178, 180,181,202,97
NH_4I	18			0.489		0.484														m.b.	202
NH_4NO_3	25					0.513														m.b.	162
$NdBr_3$	25		0.4602	0.4533	0.4442	0.4328														m.b.	45
$NdCl_3$	25		0.4629	0.4574	0.4500	0.4392														m.b.	217,206
$NiBr_2$	18		0.394	0.391	0.388						(2.5)									Hitt.	172
$NiCl_2$	20										0.320	0.264	0.200	0.191	0.189					s.o.	152,172
$Pb(NO_3)_2$	25				0.487	0.487														Hitt.	183
$PrBr_3$	25		0.4574	0.4531	0.4426															m.b.	217
$PrCl_3$	25	0.4664	0.4636	0.4587	0.4502	0.4396														m.b.	45
RbBr	18			0.495		0.492														m.b.	197
RbCl	18			0.497		0.494														m.b.	197,178,180,181,202
RbI	18			0.498		0.497														m.b.	197,86,212
$SmCl_3$	25		0.4634	0.4571	0.4425	0.4398														m.b.	45,176,178,180,181, 198,202,206
$SrBr_2$	18			0.410		0.392														m.b.	203
$SrCl_2$	25			0.424	0.415	0.405	0.393	0.370	0.343	0.322	0.306	0.287	0.274	0.276						e.m.f.	49,171
SrI_2	18			0.416		0.393														m.b.	203
$ThCl_4$	20			0.10	0.24	0.24	0.24	0.24	0.24											Hitt.	36
TlCl	25					0.481														m.b.	178,180,181,207
$TlClO_4$	25				0.531	0.533	0.534													e.m.f.	207
TlF	25					0.481														e.m.f.	207
$TlNO_3$	17					0.512														Hitt.	272,273
	25					0.516														e.m.f.	207
TlOAc	25					0.656														e.m.f.	207
$Tl_2(SO_4)_3$	18			0.475	0.475	0.475														Hitt.	172,178,180,181,183, 198,274
	25					0.468														e.m.f.	207
UO_2Cl_2	20								0.268	0.237	0.217	0.191								s.o.	275
	40								0.281	0.241	0.223	0.218								s.o.	275
	60								0.285	0.247	0.233	0.234								s.o.	275
$UO_2(NO_3)_2$	25	0.19	0.23	0.33	0.18	0.16	0.02	(0.15)												Hitt.	276
$YbCl_3$	25		0.4496	0.4461	0.4345	0.4235														m.b.	45
$ZnBr_2$	25				0.383	0.366	0.349	0.324	0.305	0.294	0.284	0.216	0.032	—0.108	—0.168	—0.284	—0.336		—0.563	e.m.f.	277,198,205,211
	40		0.4076	0.4073	0.4044	0.3894														m.b.	191
$ZnCl_2$	20						0.365	0.345	0.306	0.258	0.207	—0.09	—0.128	—0.220	—0.296	—0.417	—0.444			s.o.	12,172,198,211,278, 279
	40							0.320	0.195	0.105	0.025	—0.108	—0.306	—0.377	—0.425	—0.512	—0.550			s.o.	12
	60							0.348	0.248	0.188	0.136	0.05	—0.108	—0.183	—0.253	—0.400	—0.470			s.o.	12
	80							0.360	0.270	0.210	0.156	0.066	—0.092	—0.163	—0.212					s.o.	12
$Zn(ClO_4)_2$	25						0.409		0.361		0.325	0.317	0.291	0.281	0.275	0.271	(8.0)			e.m.f.	88
ZnI_2	25					0.382	0.363	0.336	0.320	0.308	0.291	0.236	0.115	0.056	0.040	—0.116	—0.19	—0.291	—0.55(20)	e.m.f.	88,205,211
$ZnSO_4$	20				0.364	0.361	0.356	0.347	0.334	0.321	0.309	0.240	0.222							Hitt.	202, 19—25, 203, 205,280
»	25					0.392	0.392	0.350	0.301	0.276	0.267	0.230	0.165							e.m.f.	204,208,281

by measuring the quantity of matter in the column. The accuracy of the results obtained by this method is 2–3%.

Data on transport numbers and mobilities in mixed solutions are few, and mostly of a tentative nature.

VI. EXPERIMENTAL DATA ON TRANSPORT NUMBERS IN AQUEOUS SOLUTIONS OF ELECTROLYTES

Many papers on the measurement of transport numbers, by different methods, have been published. Collected tables of transport numbers have appeared in many works of reference [171–174]. The fullest information, relating both to aqueous and to non-aqueous solutions of electrolytes, is to be found in Landolt and Börnstein's Tabellen [171]. However, these data are difficult to use, because the experimental results are reported uncritically. Furthermore, a significant volume of recent work, dealing mainly with concentrated aqueous solutions of electrolytes, has not yet found its way into standard tabulations. In the Russian literature tables of transport numbers can be found in "Spravochnik Khimika" (The Chemist's Handbook) [174] and in "Spravochnyi Tom Tekhnicheskoi Entsiklopedii" (Reference Volume of the Technical Encyclopaedia) [173]. However, the results given in those tabulations are based on early measurements of transport numbers in aqueous solutions of electrolytes, and do not provide a balanced account of recently developed new methods, or of the results obtained thereby.

Experimental values of the transport number for a given electrolyte are usually in marked disagreement. For dilute solutions, the discrepancies are relatively small: their causes have been discussed in the literature many times [2,3,36,117,172]. In the region of high solution concentrations the scatter of results is often very large [12,39,75]. For this reason, we adopted the following precedure to construct a general table of the transport numbers of cations in aqueous electrolyte solutions (Table 1) and a table of transport numbers for aqueous solutions of mixtures of electrolytes (Table 2):

(a) For each compound, the results covering the widest range of concentrations and temperatures were tabulated.

(b) When the results obtained by different methods in the same range of concentrations and temperatures showed serious disagreement, measurements by the moving boundary method were selected for the low-concentration region and measurements by the simultaneous observation method for the high-concentration region.

(c) In the few cases where the results obtained by different methods for a given compound were in good agreement, the values were combined.

The first column in Table 1 lists the chemical compounds. The second column gives the temperature at which the measurements were made. The concentration range from 0.005 N to 15 N is divided into 15 intervals; concentrations are expressed in equiv. litre^{-1} (N). Values of the transport number at intermediate concentrations, not given in the original paper, were found by graphical interpolation. Anion transport numbers were recalculated as cation transport numbers, assuming that $T_c + T_a = 1$. Figures in brackets denote the concentration corresponding to the transport numbers tabulated underneath. The column headed "method" indicates the method of measurement used, with the following abbreviations: Hitt. for Hittorf's method, e.m.f. for the e.m.f. method, m.b. for the

TABLE 2. Cation transport numbers in aqueous electrolyte solutions.

Substance: component I	Substance: component II	T, °C	Concentration, N: c_1	Concentration, N: c_2	$T_{M^+}(1)$	$T_{M^+}(2)$	Method	Literature references
$BaCl_2$	HCl	18	0.05	0.05	0.0955	0.648	Hitt.	160
$BaCl_2$	KCl	18	0.05	0.05	0.191	0.271	Hitt.	160
$CaCl_2$	HCl	25	0.000	0.100		0.8314	m.b.	120
			0.025	0.075		0.7619		
			0.05	0.05		0.6518		
			0.075	0.025		0.4537		
$CaCl_2$	LiCl	20	0.1	5.0	0.0028		m.c.	169
			0.12	6.0	0.0014			
			0.16	8.0	—0.0048			
			0.20	10.0	—0.011			
			0.24	12.0	—0.0093			
CsCl	NaCl	25	0.1	1.9	0.026		Hitt.	161
			0.05	1.95	0.014			
			0.2	3.8	0.026			
			0.1	3.9	0.013			
		20	0.05	5.0	0.0038		m.c.	169
			0.06	6.0	0.0020			
			0.07	7.0	0.0009			
			0.08	8.0	0.0002			
			0.09	9.0	—0.0007			
			0.1	10.0	—0.0012			
$CuCl_2$	LiCl	20	0.04	4.0	0.00007		m.c.	169
			0.06	6.0	—0.0014			
			0.08	8.0	—0.0032			
			0.1	10.0	—0.0050			
			0.12	12.0	—0.0042			
			0.04	2.0	0.0055			
			0.07	3.5	0.0019			
			0.1	5.0	—0.0001			
			0.13	6.25	—0.0035			
			0.17	8.5	—0.0061			
			0.215	10.75	—0.0102			
			0.25	12.50	—0.0083			
		20	0.20	5.0	0.0025		m.c.	168
			0.24	6.0	0.0074			
			0.32	8.0	—0.0027			
			0.40	10.0	—0.0077			
			0.48	12.0	—0.011			
		40	0.11	5.5	—0.0032			
			0.17	8.5	—0.012			
		60	0.10	5.0	0.0015			
$CuCl_2$	LiCl	60	0.14	7.0	0.0000		m.c.	168
			0.16	8.0	—0.0030			
			0.20	10.0	—0.0061			
			0.24	12.0	—0.0062			
HCl	KCl	17	0.1123	1.978	0.116	0.400	Hitt.	167
		18	0.0999	0.1005	0.637	0.123		
			0.1060	0.2509	0.475	0.220		
			0.1042	0.509	0.337	0.307		
			0.1020	1.008	0.191	0.380		
			0.1105	2.685	0.074	0.464		
		20	0.1129	3.100	0.074	0.457		
		25	0.075	0.025	0.7456	0.0503	m.b.	117,160
			0.05	0.05	0.6198	0.1242		
			0.025	0.075	0.4109	0.2477		
HCl	LiCl	17	0.0998	0.3074	0.476	0.148	Hitt.	167
		20	0.1165	0.0888	0.705	0.055		
			8.0	0.16		0.0020	m.c.	170
			9.0	0.18		0.0002		
			10.0	0.20		0.0008		
			11.0	0.22		0.0022		
HCl	NaCl	14	0.1055	1.905	0.232	0.266	Hitt.	167,157
			0.15	0.05	0.770	0.0333		
		20	0.1005	0.0967	0.662	0.086		
			0.1081	2.272	0.111	0.347		
HCl	NaCl	21	0.0977	1.019	0.392	0.208	Hitt.	167,157
			0.0944	1.900	0.119	0.310		
			0.1041	4.332	0.049	0.330		
KCl	LiCl	25	0,050	0.050	0.2774	0.1435	m.b.	166
			0.1	1.9		0.036	Hitt.	161
			0.05	1.95		0.019		
			0.2	3.80		0.036		
			0.1	3.90		0.022		
KCl	NaCl	25	0.798	0.202	0.368	0.063	Hitt.	158
			0.745	0.254	0.372	0.084		
			0.664	0.336	0.338	0.109		
			0.517	0.493	0.262	0.169		
			0.491	0.509	0.256	0.157		
			0.322	0.678	0.159	0.246		
			0.224	0.776	0.129	0.239		
			0.198	0.802	0.108	0.288		
			0.2	1.8	0.057		Hitt.	161,291
			0.08	1.92	0.019			
			0.04	1.96	0.010			
			0.10	3.9	0.017			
			0.20	3.8	0.038			
			0.2	4.8	0.025			
			0.50	4.5	0.052			
NaCl	RbCl	25	1.9	0.10		0.034	Hitt.	161
		25	1.95	0.05		0.017		
			3.8	0.20		0.031		
			3.9	0.10		0.015		

moving boundary method, s.o. for the method of simultaneous observation for the motion of the ions and of the solution, centr. for the method based on e.m.f. measurements in a gravity cell.

Column 1 of Table 2 lists the components of the mixture of aqueous electrolyte solutions, column 2 lists the temperatures. Columns 3 and 4 give the concentrations of the components (in equiv. litre^{-1}) in the order in which the components appear in column 1. Columns 5 and 6 give the transport numbers of the cations of the components, in the same order. The abbreviations used to indicate the method are the same as for Table 1. The abbreviation m.c. refers to the method of measuring transport numbers of minor constituents. The last column in both tables lists the literature references: the first number quoted is the paper from which the tabulated values were taken, other numbers refer to independent studies of the same compound.

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AZIRIDINE: SYNTHESIS, STRUCTURE, PROPERTIES

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I. INTRODUCTION

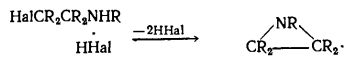
Aziridine and its derivatives have a number of very interesting physical, chemical, and biological properties, and they are attracting increasing attention of workers in different specialities. In addition to their theoretical and scientific interest, aziridine, some of its derivatives, and polyaziridine have found considerable practical uses. The object of the present review is to discuss briefly the main methods of synthesis, features of molecular structure and properties, and the chemical reactivity of aziridine together with its main uses in medicine and technology.

II. METHODS OF SYNTHESIS OF AZIRIDINE

The overwhelming majority of known methods of synthesis of aziridine and its derivatives may be divided according to reaction type into four groups of methods, leading to closure of a three-membered heterocycle: (1) intramolecular condensation reactions with elimination of the elements of an acid; (2) thermolysis of other nitrogen-containing heterocycles; (3) cyclisation reactions of nitrogen-substituted derivatives (oximes, hydrazones, dichloroamines); (4) addition reactions to C=C or C=N bonds.

Intramolecular condensation reactions. Aziridine was first synthesised by Gabriel in 1888 by the action of moist silver oxide on β-bromoethylamine hydrobromide[1]. Gabriel erroneously ascribed the structure of vinylamine to the compound obtained. This error was corrected by Marckwald, who showed that the product obtained by Gabriel was a secondary amine with a cyclic structure[2-4]; at the same time the true mechanism of

Gabriel's reaction for the cyclisation of β-halogenoethylamines, which is quite general, was discovered:

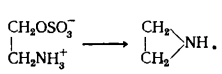


Thus, a whole series of free β-halogenoethylamines [5,6], *bis*-(β-chloroethyl)amine [7,8], and even *tris*-(β-chloroethyl)amine [9], are smoothly cyclised in aqueous, aqueous-alcoholic, or aqueous-acetone solutions with the formation of the corresponding aziridinium halides, which are then gradually hydrolysed with ring opening. In the absence of strong nucleophilic agents ($S_2O_3^{2-}$, HCO_3^-), aziridinium ions are comparatively stable and may accumulate in solutions in considerable quantities†. They may be detected titrimetrically (thiosulphate) and separated either as the poorly soluble picrates [12] and picrylsulphonates [6], or as free bases obtained by the addition of alkaline agents (Gabriel's reaction).

The rate of cyclisation of halogenoalkylamines depends on the nature of the halogen atom and the character of the substitution at both reactive centres of the molecule, the nitrogen atom and the carbon atom carrying the halogen. It increases in the order Cl < Br < I. [10] The negative inductive effect of the sulphonyl and acetyl groups in 2-chloro-3-sulphonamidobutane [13] and 1-bromo-1-acetyl-2-phenylamine [14] facilitates ring closure to such a degree that it occurs spontaneously with separation of the corresponding hydrogen halide. α-Methyl, αβ-cycloalkyl-, and even ββ-*gem*-dimethyl- substituents also have a favourable effect on the reaction centre [15-17]; this appears to be connected with corresponding changes in the conformations of the molecules of the initial halogenoalkylamines. The accumulation of bulky substituents, however, may cause steric hindrance at the reactive centre, preventing nucleophilic attack on the nitrogen atom, or even completely excluding cyclisation, as occurs with 1-chloro-2-(*N*-phenylamino)-1,1,2-triphenylethane [18] and 1-chloro-2-(*N*-acetyl)-1,1-diphenylethane [19].

Gabriel's reaction as a method of synthesising aziridines has been studied by various workers on numerous examples. It has been used for the preparation, apart from aziridine itself [20-27], of *N*- and *C*-alkyl- [28-35] and aryl-substituted [36-53] aziridines, bicyclic structures including the aziridine ring [33], and also *C*-acyl- [14], *C*-carboxy- [54], and *N*-sulphonyl-substituted [55-64] aziridine derivatives. It is inapplicable only in the case of *N*-acyl derivatives [65].

The second most widely used method of preparing aziridines after Gabriel's reaction is Wenker's synthesis, which is similar to it in principle [66-76]; this consists of cyclisation by the action of alkali of acid β-aminoalkylsulphates:



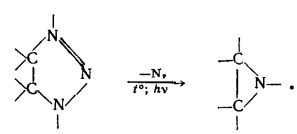
The most substantial differences between this method and Gabriel's reaction are the lower rates of cyclisation of β-aminoalkylsulphates compared with halogenoalkylamines [77]. However, since the aziridine formed remains in contact with hot alkaline solution for a longer period, the degree of hydrolytic cleavage increases and the yield correspondingly falls. A solution to the problem of the yield in Wenker's synthesis has been found by reducing the reaction time, either by increasing the reaction temperature [78], or by rapidly distilling off the aziridine formed by the slow addition of the aminoethyl sulphate to boiling aqueous alkali [79]. The yields thus obtained (up to 91%) correspond to the yields in Gabriel's reaction. The majority of industrial plants for the preparation of aziridine are based on Wenker's synthesis [80,81].

A study of the cyclisation of stereoisomeric β-halogenoalkylamines and β-aminoalkyl sulphates has shown that this is always accompanied by inversion of confirguration. Thus, the cyclisation of DL-*threo*- or L(+)-*threo*-3-aminobutan-2-ols leads to *meso*-2,3-dimethylaziridine (*cis*-isomer), but the L(+)-*erythro*-isomer gives L(-)-2,3-dimethylaziridine (*trans*-isomer) [82]. Similarly, *cis*-2,3-diphenylaziridine may be obtained by the cyclisation of *l*- or *dl*-iso-α-amino-β-chlorodibenzyls, and the *l*-*trans*- and *dl*-*trans*-isomers from *l*- and *dl*-α-amino-β-chlorodibenzyls respectively [37]. In systems in which *trans*-closure is impossible, the aziridine ring is not formed. Thus, when the stereoisomeric α-aminocyclohexyl sulphates are treated with alkali, only the *trans*-isomer gives an aziridine derivative (tetramethyleneaziridine) [83].

A large number of syntheses (mainly of various *C*-acyl substituted derivatives of aziridine) proceed in the same way as the Gabriel–Wenker reaction: vicinal dihalogeno-ketones [84-91], -ethers [92-94], -nitriles [95-97], or α-halogeno-substituted αβ-unsaturated ketones [98-100] and ethers [101-104] react with ammonia and amines, and there is also the analogous reaction of αβ-unsaturated ketones with iodine complexes of ammonia and amines [105,106]. The reaction with ammonia leads to aziridine derivatives unsubstituted at the nitrogen; the reaction with primary amines leads to substituted derivatives; and the reaction with secondary amines leads to the corresponding quaternary aziridinium compounds [99,100].

These reactions can be described in the most general way as cyclisation of bifunctional compounds of the type $(R_2CX)_2$ (R = H or a hydrocarbon group and X is a halogen atom, or a sulphate, nitrate, or other polar group) by ammonia or amines in the presence or absence of acid acceptors. One of these reactions — the condensation of dichloroethane with ammonia in the presence of calcium oxide — has proved such a successful method of synthesising aziridine that immediately after its discovery it was used on a production scale by the Dow Chemical Co. [107-109]. Experts of this firm consider that the successful development of the production of aziridine by this method will lead to a very considerable reduction in its cost in a short time [110].

Thermolysis of nitrogen-containing heterocycles. As in the synthesis of cyclopropanes by Kishner's method, thermal [111-116] or photolytic [117] decomposition of 1,2,3-triazolines leads to aziridine derivatives:

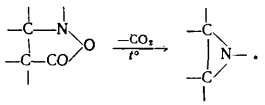


Evidently, the analogy in the structure of two strained rings may be extended to the thermolysis mechanism. In

† Since aziridine derivatives have an extremely high biological activity, the amount of aziridinium ions produced by decomposition is also reflected in the biological activity of the solutions [10,11].

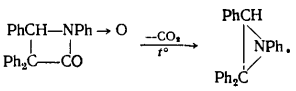
contrast to the pyrolysis of pyrazolines, which presupposes preliminary prototropic displacement of the double bond to the 1,2-position (catalysed by alkali), thermal decomposition of dihydrotriazoles, containing the ready-made azo-group in their ring, does not require the use of an alkaline catalyst.

A very similar thermolytic route is known for another five-membered heterocycle, oxazolid-2-one[118-120]:



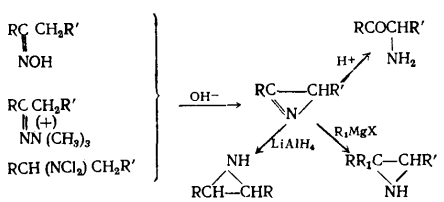
The two methods differ in that in the first contraction of the ring is accompanied by elimination of the azo-group as a nitrogen molecule, whereas in the second the $-C\overset{O}{\underset{O-}{<}}$ fragment of the lactam ring is removed as a molecule of carbon dioxide. Although simple heating is sufficient for decomposition of triazolines, pyrolysis of oxazolid-2-ones must be carried out in the presence of an alkaline solvent, since the carbon dioxide eliminated may react with the aziridine.

Mention should also be made of the formation of polyphenylated aziridine (1,2,3,3-tetraphenylaziridine) on heating the product of the addition of diphenylketene to benzaldehyde *N*-phenyloxime[18]:



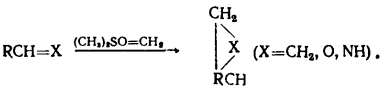
An attempt to prepare other aziridine derivatives in a similar way proved unsuccessful.

Cyclisation of oximes, hydrazones, and chloramines. The rearrangement of some derivatives of oximes (tosylates[121,122], magnesium halides[123-129]) and hydrazones (methyliodides of dimethylhydrazones[130]) of the structure $RC(=NX)CH_2R'$, where X = OH or $^+N(CH_3)_3$, and also *NN*-dichloro-s-alkylamines[131,132] of similar structure, to α-amino-ketones and -alcohols:

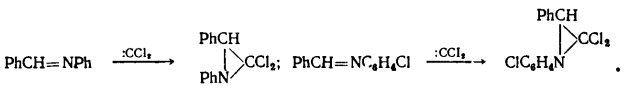


leads to common cyclic intermediate products, the corresponding azirines or alkoxyaziridines. Reduction of the latter with lithium aluminium hydride or Grignard reagents and the use of mild conditions for hydrolysis of the reaction products (ice + ammonium chloride) enabled the rearrangements mentioned to be used as a method of synthesis of the corresponding substituted aziridines.

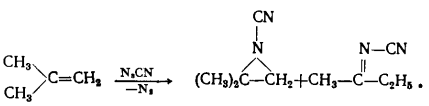
Addition to C=C and C=N bonds. Cyclisations by addition to C=C or C=N bonds include a number of recently discovered reactions in which the C=N bonds of imines, which are susceptible to nucleophilic attack, are methylenated, and reactions in which activated alkene C=C bonds are iminated with the aid of unstable and extremely active compounds of radical or ionic character. Thus, it has very recently been shown that sulphonium ylides, formed by the decomposition of the corresponding sulphonium salts by strong alkalis in anhydrous dimethylsulphoxide, react with polar C=C, C=O or C=N bonds to give good yields of derivatives of cyclopropane, ethylene oxide and aziridine respectively[133-136]:



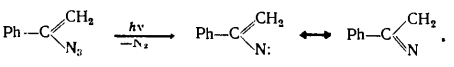
An analogous route is also known for radical reagents, carbenes and their nitrogen analogues — nitrenes or azocarbenes. The addition of hydrocarbon carbenes to C=N bonds of imines[137,138], or of azocarbenes to alkene C=C bonds[139,140] unambiguously leads to derivatives of aziridine, for example,



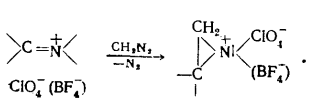
Since nitrenes are produced by the thermal or photolytic decomposition of azides, this mechanism is obviously also the basis of the synthesis of aziridine derivatives described in the literature in which alkenes react directly with certain azides (sulphonyl azides[141-143], cyanazide[144], and carbamoyl azide[145]), for example:



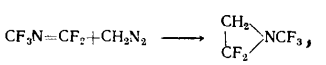
Apart from adding to multiple bonds, some nitrenes can undergo intramolecular cyclisation reactions[146-148]. For example, photolysis of t-butylazide and α-azidostyrene gives good yields of 2,2-dimethylaziridine[146] and 2-phenylazirine[147]:



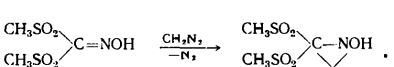
Diazomethane is another widely used methylenating agent; the addition of diazomethane to C=N bonds of imines gives triazolines, which are starting materials for the synthesis of aziridines by thermolysis (see above). In the case of tertiary iminium salts with weakly nucleophilic anions (perchlorates and fluoroborates) similar nucleophilic attack of diazomethane leads directly to the corresponding aziridine derivatives in high yield[149-152]:



Polyfluorinated imines react in a similar way, for example[153]:

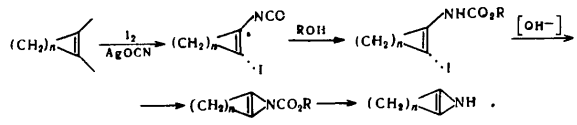


and also *bis*-methanesulphonylisonitrosomethane[154]:



Mention should also be made of the synthesis of condensed aziridines from cyclic alkenes (mainly in the

steroid series) by hydrolysis of the corresponding iodocarbamates, obtained by the reaction of alkenes with iodine in the presence of an excess of silver cyanate[155,156]:



III. STRUCTURE AND PROPERTIES

Physical properties. Closure of the three-membered C–C–N heterocycle is accompanied by a considerable increase in boiling point, specific gravity, and some other physical constants connected with intermolecular interactions (Table 1).

This effect is connected with the increased strength of H–N...H-hydrogen bonding (both in comparison with non-cyclic analogues and in comparison with isologues), which is characteristic of aziridine.

Thermochemical properties. The following are the main thermochemical values for aziridine:

		kcal mole^{-1}
Heat of combustion	C_2H_5N(liq.)	380.34 ± 0.15
Heat of formation	C_2H_5N(liq.)	21.96 ± 0.14
Heat of formation	C_2H_5N(gas)	26
Heat of evaporation	C_2H_5N	4

Comparison of the given experimental values[109,160] for the energy of formation of aziridine with those calculated from the summation of the bond energies (12 kcal mole^{-1}) gives a value of 14 kcal mole^{-1} for the strain energy of the three-membered heterocycle.

Solubility and properties of aqueous solutions. Examination of the three-component system aziridine–water–sodium hydroxide is of considerable practical interest. The relevant ternary diagram (Fig. 1) gives valuable information on the division into and composition of phases in this system[161]. Here each point inside the region bounded by the binodal curve and the upper tie-line corresponds to a system divided into two liquid phases. Their composition can be determined from the points of intersection of the corresponding tie-lines with the binodal curve and the base of the triangle.

Detailed study of the dependence on concentration of density, refraction, melting point, boiling point, surface tension, and viscosity of aqueous solutions of aziridine shows that all these undergo sharp changes at the point with an aziridine : water ratio of 1 : 2.[161] The nature of these changes (minima, breaks, and points of inflexion on the curves) indicates the formation of a characteristic chemical compound of aziridine and water of this composition. Infrared spectroscopic examination of the 1 : 2 compound of aziridine and water shows that the characteristic

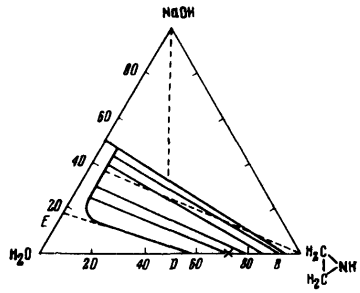


Fig. 1. Ternary diagram of the aziridine–water–sodium hydroxide system at 20°.

frequencies of aziridine are absent and suggests a cyclic chelate hydrate structure formed by intermolecular OH- and NH-bonding. It is interesting to note that the parachor and thermochemical properties of this compound also indicate that the three-membered heterocycle in it must be opened‡.

Molecular structure. As with cyclopropane, closure of the three-membered C–C–N ring is accompanied by considerable distortion of the valence angles, which in turn leads to the development of substantial ring strain. Clearly this strain is primarily reflected in the molecular structure of aziridine, that is, in bond energies, interatomic distances and angles, etc. Such methods as spectroscopy, microwave spectroscopy, mass spectroscopy, and electron diffraction give interesting information on this point. Thus, analysis of the microwave spectrum of aziridine shows that the imine hydrogen (NH bond) of aziridine does not lie in the plane of the ring[162–165]. Comparison of the experimental intensity of the bands with the calculated intensity confirms that the molecule is not coplanar. Structural parameters of the molecule and values of the components of the dipole moment (Table 2) have been determined from the microwave spectrum of aziridine[166,167].

The values in Table 2 agree with those calculated from electron-diffraction data[168].

Some conclusions on the structure of the aziridine molecule may also be drawn from an analysis of its infrared and

TABLE 2. Structural parameters of the aziridine molecule (from microwave spectroscopic data).

Bond	Bond length, Å	Angle	Value of angle	Component μ	Value of μ (D)
C–C	1.480	C_2NH	112°	μ_a	1.670
C–N	1.488	H_2CC	159°45′	μ_c	0.890
C–H	1.083	HCH	116°41′	μ_{total}	1.890

TABLE 1. Physical properties of aziridine and dimethylamine.

Compound	B.p., °C	M.p., °C	d_4^{20}	γ, dyn cm^{-1}	η, cP	Flash-point, °C	Refs.
Aziridine	55–56	−78.0	0.837	32.8	0.418	−11.1	157,158
Dimethylamine	7.4	−96.0	0.680	18	0.37	—	159

‡ Similar results obtained by workers by the Dow Company are given in the prospectus of this company published in 1965. This also gives some original physical constants of aziridine, and also recommendations for its transport and storage together with safety precautions for working with it, and the stability of various constructional materials in contact with aziridine.

Raman spectra[169-174]. The presence of increased (3012–3078 cm^{-1} compared with 2800–2980 cm^{-1} in aliphatic amines) CH stretching vibration frequencies indicates considerable strain in the three-membered heterocycle. The ring strain in aziridine leads to an increase in the polarity of the NH bond and to some reduction in its characteristic vibration frequencies compared with aliphatic amines[175]. This fact is in agreement with the low basicity constants of aziridine and its derivatives. A considerable shift in NH frequencies (from 3357 to 3280 cm^{-1}) in liquid compared with gaseous aziridine is explained by intensive NH...H-hydrogen bonding[176]. Deformation vibrations of the ring in the 1210 and 857–820 cm^{-1} regions, also noted in the spectra of cyclopropane and ethylene oxide, agree with calculations based on a triangular model consisting of three parts. Examination of the vibrational spectra of substituted aziridine derivatives shows that these frequencies sharply change in intensity and are even displaced when hydrogen atoms in the ring are replaced[177,178].

The dipole moment of aziridine, calculated from the results of measurements of the dielectric constant of a benzene solution, is 1.73 ± 0.1 *D*.[179] The component WKB constants for aziridine are x_{aa} = 0.69 mc/s; x_{bb} = = 2.17 mc/s; x_{cc} = -2.86 mc/s.[180]

The ionisation potential of aziridine, determined by mass spectroscopy, is 9.94 ± 0.15 eV.[181,182]

Stereoisomerism. As with cyclopropane, the planar structure of the aziridine ring leads to the existence of two (*cis*- and *trans*-) geometric isomers for 2,3-disubstituted derivatives. As in the case of cyclopropane, the internally compensated *cis*- form is optically inactive (*meso*-form), but the *trans*-isomer and also the *C*-monosubstituted derivatives may be separated into optical antipodes. The isomeric aziridines differ somewhat in physical constants. Differences between the geometric isomers in their ability to transfer strain between two unsaturated groups are also interesting. *Cis-trans*-isomerisation of 2,3-disubstituted aziridine is catalysed by irradiation or by dry hydrogen chloride[183].

Still another form of stereoisomerism of aziridine derivatives is connected with the presence of a nitrogen atom in the ring. The existence of optical isomers, due to the asymmetry of the tervalent pyramidal nitrogen, in *N*-substituted aziridine had long been suspected[184], but it has only recently been demonstrated definitely by nuclear magnetic resonance, which showed the presence of two triplet resonances of ring protons[185-189].

Electronic structure. Since two hybrid atomic *sp*-orbitals cannot form an angle of less than 90° with each other, the structure of the three-membered rings of cyclopropane, ethylene oxide, and aziridine cannot be explained by Pauling's hypothesis of directed valencies. In this case it must be assumed that the corresponding bonding orbitals are not aligned directly one towards the other, as this hypothesis requires, but are bent to form "banana" bonds (Fig. 2).

To form a ring, hydrocarbon atoms use their hybrid $(2s-2p)\sigma$-orbitals (at an angle of 92°).[190] This type of bonding is intermediate between lateral π-bonding and terminal σ-bonding modes of overlap[191-193]. Less overlap of the bent bonds is compensated by less distortion for the orbitals with less bending. Theoretical calculations show that these orbitals of the ring now become $sp^{4,12}$-orbitals instead of the usual tetrahedral sp^3-orbitals[194,195]. A study

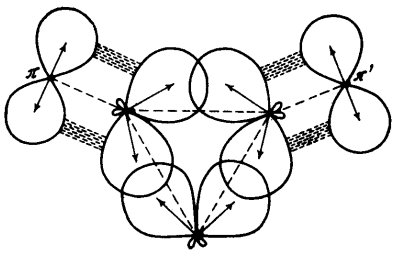


Fig. 2. Electronic structure of the aziridine molecule (plane projection: π and π' atoms, containing *p*-electrons, linked to both carbon atoms of the ring).

of the molecular structure of aziridine shows that the $sp^{4,12}$-bonds formed are shorter than normal single C–C or C–N bonds. The strong *p*-character of the *endo*-orbitals of the ring leads to a strong *s*-character of the external bonds ($sp^{2,28}$-*exo*-bonds). These bonds form an angle of 116° with one another, which exceeds the value of 109.5° for the tetrahedral angle. This strained structure is reflected in all the properties of compounds with a three-membered ring. The most important of these is overlapping (shown dotted on Fig. 2) of the deformed bonds of the ring with the *p*-orbitals of substituents (for example, a double bond or benzene ring) or free electron pairs of halogen atoms, known by the term conjugation.

A quantitative evaluation of conjugation with the aziridine ring is given by a comparison of Hammet's σ constants for ethylenimino-, dimethylamino-, and amino-groups, calculated from chemical shifts of the fluorine (^{19}F) signal in the NMR spectra of the corresponding *m*- and *p*-fluorophenylamines[196].

Ethylenimino-group	σ_{para} = + 0.066	σ_{meta} = −0.290
Dimethylamino-group	+ 0.098	−0.530
Amino-group	+ 0.115	−0.486

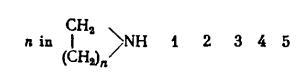
This comparison shows that, although the inductive effect of the three-membered heterocycle is close to the effects of non-cyclic groups, the capacity of its nitrogen atom for conjugation with the benzene ring is greatly reduced. This effect of the inclusion of the nitrogen atom in the three-membered ring is connected with a reduction of overlapping of rehybridised *endo*-orbitals of quadrivalent nitrogen with the π-orbitals of the benzene ring.

The position of aziridine in the cyclic imine series. In the series of cyclic imines the strained three-membered ring of aziridine occupies a special place. Thus, in the infrared spectra, a gradual shift of the upper limit of C–H bond frequencies (from 2919 cm^{-1} for hexamethyleneimine to 3078 cm^{-1} for aziridine) occurs on going from rings with a large number of atoms, in which there is no material strain, to strained three- and four-membered rings[197]. The N–H frequencies change in the reverse order (with increasing strain in the ring the N–H frequencies are reduced) and the basicity of the cyclic imines increases.

Comparison of the ultraviolet absorption intensities of *N*-phenylsubstituted cyclic imines and dimethylaniline in the 250 and 290 mμm§ regions shows that the conjugation energy of the nitrogen atom with the benzene ring increases

§ Linearly related to benzene ring–nitrogen delocalisation interaction.

in higher cyclic imines and dimethylaniline compared with aziridine[198]. In the same way, there is a regular reduction in ionisation potential as the ring increases in size:



and also in the stability of the corresponding complexes with trimethylboron[199].

These facts are most generally and basically reflected in the chemical shifts of the NMR spectra of cyclic imines. Results obtained show that the nitrogen atom of the three-membered ring has the minimum electron density[200]. It would be expected to have the minimum capacity for adding a proton and therefore the minimum basicity.

IV. REACTIONS OF AZIRIDINE AND ITS DERIVATIVES

All the diverse reactions of aziridine and its derivatives may be divided into two approximately equally large groups. The first of these comprises reactions in which only the free electron pair of the nitrogen atom participates and aziridine behaves simply as an amino-compound. The basic feature of reactions of this type is the relative ease with which they are transformed to reactions of the second group, because of the instability of the strained three-membered heterocycle. In this connection they require special precautions in that acids and strong nucleophilic reagents must be absent.

Reactions of the second group, which lead to opening of the three-membered heterocycle, constitute the most interesting feature of the chemistry of aziridine, a unique compound that combines the properties of saturated and unsaturated carbon and nitrogen atoms. Polymerisation¶ is a special ring-opening reaction; this proceeds by the step-wise stringing together of aziridine molecules by a polymer chain with an aziridinium ion at its growing end.

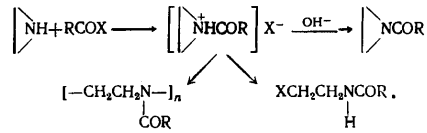
1. Reactions with Retention of the Aziridine Ring

Protonation. Potentiometric titration of aziridine with hydrochloric or perchloric acid in aqueous solutions of neutral salts has been used to determine the thermodynamic protonation constant[201-205]. The titration curves obtained in this way have the form characteristic of weak bases. Comparison of the calculated pK_a value (7.88) for aziridine with the corresponding constants for dimethylamine (10.72) and ammonia (9.25) shows a considerable reduction in the basicity of the nitrogen atom in the three-membered ring (see above)[202].

The temperature dependence of aziridine protonation has been studied and its heat of neutralisation has been determined as $\Delta H^\circ = 11.6$ kcal mole^{-1}.[206] This is lower than the corresponding value for ammonia, which also indicates the low basicity of aziridine.

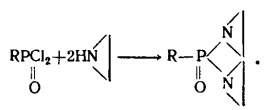
Complex formation. The ability of aziridine to act as a donor of the free electron pair of the nitrogen atom is also reflected in complex formation with transition metal ions[179,206-208]. The type of bond that aziridine forms as a ligand with metal ions and their coordination numbers in these compounds are similar to those of the corresponding ammine complexes. In agreement with the reduced basicity of aziridine, the stability of these compounds is lower than that of the analogous ammine complexes.

Acylation and alkylation. The reaction of aziridine with acid anhydrides or acid chlorides leads to the corresponding *N*-acylaziridines only when the acid formed is immediately removed from the site of reaction with some acid acceptor[209-214]. Otherwise the *N*-acylaziridinium compounds formed undergo further conversion with ring opening and the formation of substituted β-acylethylamides or their polymers:



The *N*-acylaziridines obtained in this way are very unstable compounds[210]. Some of them have interesting biological properties and are used industrially. Special mention should be made of tris-(1-aziridinyl)-*s*-triazine[215-217] (triethylenemelamine or TEM), the first aziridine preparation that was found to have a therapeutic effect in the treatment of cancer and sarcoma[218]. This discovery at once led to numerous syntheses of other aziridine derivatives of triazine and some heterocyclic systems, such as pyrimidine, purine, tetrazine, and others of similar structure.

The reaction between aziridine and phosphorus oxychloride formed the basis of the most numerous class of anti-cancer compounds of aziridine, the aziridinylphosphine oxide derivatives[219,220]. The possibility of varying their properties was discovered by first introducing a substituent (or two substituents) into phosphorus oxychloride and then treating it with aziridine[221]:



An analogous series of aziridinylphosphine sulphides based on the acid chlorides of thiophosphoric and thiophosphonic acids has been obtained[222,223].

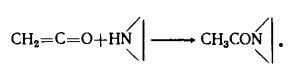
A recently proposed method of acylating aziridines differs in principle from the reactions considered[224]. It starts directly from aziridine and the corresponding free acid and does not require the use of alkaline agents. In this method *NN*-dicyclohexylcarbodiimide is used as a unique dehydrating agent. This method is particularly convenient in the preparation of amino-acyl aziridines; it is also applicable to carboxylic and sulphonic acids.

Since, as a rule, alkylation of amines requires more drastic conditions than acylation, its application to aziridine does not usually give individual monomeric *N*-alkylaziridines; the successful use of alkylation is limited to a few reactions with the most active alkyl halides[215,225]. It is interesting to note that the aziridine ring, stabilised by two alkyl substitutents at the ring carbon atoms[226] or by inclusion in the bicyclic structures of tetramethyleneaziridine[227] and spiro-cyclohexylaziridine[228], can be

¶ Polymerisation of aziridine and the properties of polyaziridine, see Uspekhi Khim., 34, 1249 (1965) [Russ.Chem.Rev., 515 (1965)].

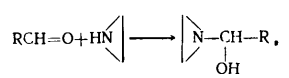
normally alkylated and even gives stable quaternary aziridinium compounds on reaction with an excess of alkyl halides.

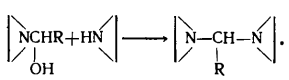
Addition to multiple bonds. While these reactions lead to products considered in the previous section, they proceed much more smoothly, because they are not accompanied by the elimination of any acid or nucleophilic compounds. Thus, the addition of aziridine to the C=C bonds of ketones gives the corresponding 1-acylaziridines in nearly quantitative yield[229,230], for example,



Similarly, aziridine readily adds to the activated double bonds of esters[231-234] and nitriles[235-237] of $\alpha\beta$-unsaturated acids; in the presence of catalytic quantities of metallic sodium, it also adds to the conjugated double bonds of dienes[238,239] and styrenes[238,240]. An analogous reaction of aziridine with quinone formed the basis of a new class of anti-tumour preparations, aziridinoquinones and hydroquinones[241,242].

The addition of aziridine to the carbonyl bonds of aldehydes and ketones at first leads to the corresponding aziridinyl carbinols, which are unstable compounds that tend to undergo polymerisation and cleavage to the starting components[215,243-248]. Aziridinyl carbinols can combine with a second molecule of aziridine, another amine or ammonia to form diaminomethanes[249-253]:

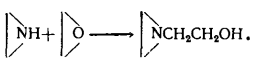




This mechanism is quite general. In the reaction of aziridine with $\alpha\beta$-unsaturated aldehydes and ketones the first stage is addition to the C=C bond[254,255]. A second molecule of aziridine combines with the C=O bond to form diaziridinyl carbinols, which have an appreciable anti-tumour effect[256].

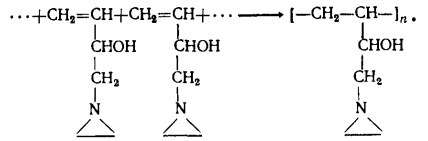
Of the addition reactions of aziridine to C=N bonds, the most widely studied is the reaction with cyanuric acid and its esters[215,257-260], which leads to aziridinylureas. Aziridinylureas, and particularly bisaziridinylureas (based on diisocyanates), are used in the textile industry for the treatment of synthetic and natural fibres and fabrics.

Addition as a result of opening of strained rings. In common with other amines, aziridine opens vigorously the three-membered rings of epoxides, adding the β-hydroxyethyl group formed to its nitrogen atom[261-263]:



Tetramin is a compound of this kind; it is the product of the addition of aziridine to divinyl monoepoxide and is the most powerful cytostat of the aziridine derivatives[264-267].

An interesting anti-cancer preparation has also been synthesised by the radical polymerisation of tetramin[268]:



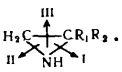
In this polymer, which is less toxic than tetramin, the aziridine rings with their anti-tumour activity are retained.

A similar reaction with thiiran has also been described[269]. Dimerisation of aziridine is an example of this reaction involving aziridine itself[270].

Of the other reactions of aziridine common to other amines, mention should be made of condensation with diborane[271], trimethylboron[199], alkali metals[272], and organometallic compounds[273], and also the formation of halogenoamines by the action of hypohalites[274-277].

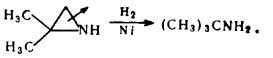
2. Reactions with Opening of the Aziridine Ring

In the general case of asymmetrically substituted aziridines a variety of products is to be expected, corresponding to three possible ways of ring opening:



Clearly, these three ways of ring opening will not always occur. Examination of the nature of the attacking reagent enables definite conclusions to be drawn as to the structure of the products formed. In this respect homolytic reactions (non-polar reagents) are distinguished from heterolytic reactions (polar reagents). All homolytic reactions rigorously follow the route predicted by rupture of the least polar bond, but the reverse does not necessarily hold for heterolytic reactions. Here the nucleophilic properties of the attacking reagent must also be taken into account. Rearrangements of aziridine derivatives that usually proceed with participation of a polar substituent in the three-membered ring form an independent group of ring-opening reactions.

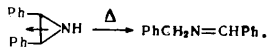
Homolytic opening of the aziridine ring. Hydrogenolysis of the three-membered ring of asymmetrically substituted aziridines proceeds exclusively homolytically at the least polar bond. Thus, the sole product of the hydrogenolysis of 2,2-dimethylaziridine (on a nickel catalyst at 130°) is t-butylamine[278-280].



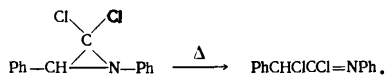
Catalytic hydrogenolysis of the three-membered heterocycle is somewhat more difficult than that of a multiple bond; the C≡N bond in β-(2,2-dimethylaziridinyl)propionitrile, or the C=C bond in *N*-vinylaziridine, can be selectively hydrogenated in the presence of the aziridine ring[235,281].

Another example of the homolytic opening of the three-membered heterocycle is thermal isomerisation of aziridine derivatives. Here the comparatively rare opening

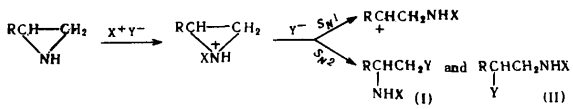
of the ring at the C–C bond corresponds to the requirement of minimum polarity of the bond undergoing homolysis, for example[282,283]:



In 2,2-dichloro-1,3-diphenylaziridine the considerable polarisation of the bonds adjacent to the CCl_2 group results in the opposite group (C–N) in the ring undergoing pyrolytic rupture[284]:

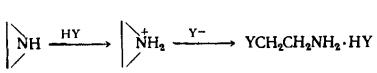


Heterolytic opening of the aziridine ring by various nucleophilic agents. When the three-membered ring in asymmetric aziridines is opened by polar reagent XY, two types of products (I) and (II) may be formed.



One of these may predominate or be formed exclusively, depending on the nature of the reagent and the substituents in the aziridine ring. Thus, in most cases hydrolysis of alkylated aziridines in acid solutions gives type (II) products, corresponding to preferential rupture of the bond at the tertiary carbon atom; ammonolysis with ammonia and amines is not so specific and leads to a mixture of products (I) and (II), and all remaining modes of nucleophilic ring opening mainly lead to products of type (I). In fact, heterolysis of the aziridine ring may proceed by two different mechanisms, depending on the nucleophilic character of the attacking reagent: (1) cationic addition, which includes protonation of the nitrogen atom, rupture of the ring with the formation of a carbonium cation, and addition of the nucleophilic agent (type S_N1 unimolecular mechanism), and (2) rupture as a result of nucleophilic attack by the anion Y^- on the protonated ring (type S_N2 bimolecular mechanism). Because of greater stability of the substituted carbonium cation, the first mechanism leads exclusively to type (II) products, but the second mechanism leads preferentially to the formation of type (I) products, because of the lower electron density of the methylene group and reduced steric hindrance to attack.

The action of acids on aziridine is accompanied by rapid opening of the protonated three-membered ring as a result of nucleophilic attack of the acid anion and addition of this anion to one of the carbon atoms of the ring with the formation of the corresponding β-substituted ethylamine:



With asymmetrically substituted aziridines the reaction leads to two isomeric products; however, in each individual case one or other of the two routes predominates. Thus, the main products of the reaction of 2-methylaziridine with hydrogen halides are β-halogenoisopropylamines[29,30]; with 2-phenylaziridine, α-isomers are preferentially formed[36,39–41].

A study of the kinetics of the opening of aziridine rings by a number of strong nucleophilic agents (see Table 3) has shown that in all the cases examined the reaction is of second order[285–288]; this means that heterolysis of the ring by strong nucleophilic agents proceeds preferentially by the bimolecular S_N2 mechanism. The most probable mechanism of these reactions is nucleophilic attack on the methylene link in the protonated aziridine ring according to the following mechanism:

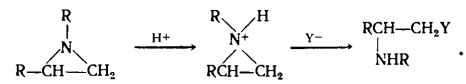
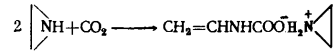


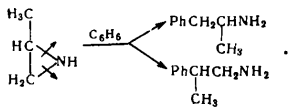
Table 3 also shows that the rate of these reactions is mainly determined by the nucleophilic character of the anion and depends to a lesser degree on substitution in the aziridine ring.

Study of the stereochemistry of the reaction of diastereoisomers of aziridines with acids shows that, as with ring closure, ring opening of three-membered aziridine derivatives is accompanied by inversion of configuration. Thus, as a result of *trans*-opening of the ring, reaction of *cis*- and L(-)-*trans*-2,3-dimethylaziridine with acetic acid gives DL-*threo*-2-acetoxy-3-aminobutane in the first case and L(-)-*erythro*-2-acetoxy-3-aminobutane in the second[289]. In the same way reaction of DL-*erythro*-3-methyl-2-phenylaziridine with hydrogen chloride gives DL-*threo*-2-amino-1-chloro-1-phenylpropane, which gives the starting aziridine when boiled with 50% potassium hydroxide[290].

Other reactions in which the aziridine ring is opened by acid agents include the unique reaction of aziridine with carbon dioxide which leads to derivatives of the unstable *N*-vinylamine[291]:



and also the aminoethylation of hydrocarbons by aziridine and its derivatives which is initiated by Lewis acids[292].



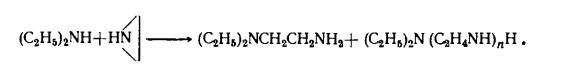
Here too asymmetrically substituted aziridines give two products corresponding to the two mechanisms of ring opening[293,294].

Such important reactions as ring opening by ammonolysis with ammonia and amines and by hydrolysis deserve special examination.

TABLE 3. Kinetics of the opening of aziridine rings by various nucleophilic agents.

Nucleophilic agent	10^6k, mole^{-1} s^{-1} at 25°			
	aziridine	2-methylaziridine	2,2-dimethylaziridine	*N*-butylaziridine
Cl^-	5.48	3.56	7.56	1
Br^-	28.5	17 8	33	8.3
CNS^-	230	145	243	110
I^-	436	168	297	—
$S_2O_3^-$	5360	5920	4880	3500

Ammonolysis. In the pure form, aziridine and most of its derivatives do not react with ammonia and amines even on prolonged heating[295,296]. In the presence of catalysts such as water, alcohols, and various acid agents (including ammonium chloride and Lewis acids) reaction occurs, leading to the formation of the corresponding ethylenediamine derivatives together with polymeric products of their further conversion[295-300]:



The ratio of ethylenediamine to polymer depends on the reaction conditions and the catalyst used. Considerable amounts of polyamines are formed in reactions catalysed by water[295-297] or ammonium chloride[298,299] at room temperature; lesser amounts are formed at increased temperature and pressure. An ideal catalyst for the preparation of ethylenediamines is aluminium chloride, which forms a stable complex with the reaction product[300].

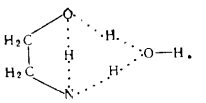
Ammonolysis of asymmetric aziridine is characterised by preferential rupture of the ring at the primary C atom, although in a number of cases considerable quantities of isomeric compounds are also formed. Thus, 2-ethylaziridine forms only one isomer with morpholine, *N*-β-aminobutylmorpholine, but with aniline a small quantity of the second isomer is formed; 2,2-dimethylaziridine forms equal quantities of both isomers with aniline[298].

The ammonolysis of "activated" aziridines without catalysts of any kind is of special interest. For most derivatives of aziridine preliminary protonation or coordination of their nitrogen atoms with a suitable Lewis acid is a condition for nucleophilic attack leading to opening of the aziridine ring, but "activated" aziridines undergo ring opening with great ease even in the absence of acid catalysts[301]. The ammonolysis of *O*-ethyl-*NN*-(1-aziridinyl)-urethane by aniline and a number of its substituted derivatives is an example of such a reaction[296]. Results of the kinetic investigation of this reaction suggest a bimolecular mechanism in which a carbon atom of the three-membered 1-aziridinylurethane ring is replaced by the amino-group of aniline.

Study of the steric course of ammonolysis shows that an overwhelming proportion of product is formed with inversion of configuration, and therefore results from *trans*-opening of the aziridine ring. Thus, DL-*threo*-2,3-aminobutane has been obtained by the ammonolysis of *meso*-2,3-dimethylaziridine with ammonia, and *meso*-2,3-diaminobutane by the reaction of L(-)-*trans*-2,3-dimethylaziridine with ammonia[302]. In the same way D(-)-*erythro*-2-amino-3-ethylaminobutane was obtained from L(-)-*trans*-2,3-dimethylaziridine by the action of ethylamine[303], and *meso*-2,2-bisethylaminobutane was obtained from L(+)-*trans*-*N*-ethyl-2,3-dimethylaziridine. In the latter case, in addition to the optically inactive *meso*-isomer, a small quantity of the optically active product, L(+)-2,3-bisethylaminobutane was observed; this corresponds to the contribution of the S_N1-reaction with frontal attack by the amine on the corresponding carbonium ion.

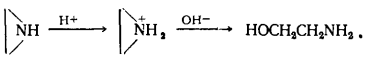
Hydrazinolysis of the aziridine ring, which is analogous to ammonolysis, has also been described[304].

Alcoholysis and hydrolysis. As has already been mentioned above, in aqueous solutions of aziridine a reaction occurs leading to the formation of a unique cyclic chelate hydrate, linked by hydrogen bonds and containing two molecules of water per molecule of aziridine[161], for example,



The addition of alkali suppresses this reaction, and heating of the solution converts the chelate hydrate in to a mixture of ethanolamine and water.

In acid solutions the mechanism of hydrolytic opening of aziridine rings is essentially different. Here the three-membered ring, previously protonated by acid, is opened as a result of nucleophilic attack of the hydroxide ion:



In the absence of catalysts, alcohols do not generally react with aziridine, but in the presence of strong acids or boron trifluoride, acid alcoholysis, similar to hydrolysis, occurs with the formation of the corresponding β-amino-ethers:

Numerous attempts to study the acid hydrolysis of aziridine derivatives under the action of aqueous hydrochloric acid have not given definite results, because of the competition between chloride ions and water molecules for opening of aziridine rings in aqueous hydrochloric acid solutions[306-309]. The ratio of the products obtained (four) largely depends on the reaction conditions.

Hydrolysis uncomplicated by other nucleophilic ring-opening reactions can only be studied for reactions catalysed by acids with very weakly nucleophilic anions (for example perchloric, picric, or fluoroboric acid) incapable of this kind of competition to an appreciable degree. The work of Clapp on the hydrolysis of aziridine, 2-ethylaziridine and 2,2-dimethylaziridine by a solution of perchloric acid is an example of this kind of reaction[286]. Study of the kinetics, activation energies, and entropies and also the composition of the products of these reactions shows (Table 4) that, although with 2,2-dimethylaziridine and 2-ethyl-2-phenylaziridine hydrolysis is mainly a unimolecular process, both uni- and bimolecular mechanisms operate with 2-ethylaziridine, and aziridine is probably hydrolysed exclusively by an S_N2 mechanism[310].

Table 4 shows that 2-ethyl-2-phenylaziridine is hydrolysed at the fastest rate. The rate of the S_N2 reaction at the primary carbon of aziridine is approximately equal to the overall rate of the S_N1 and S_N2 reactions at the secondary carbon of 2-ethylaziridine, but appreciably less

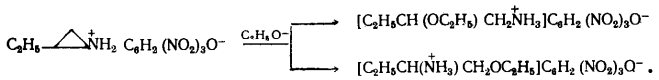
TABLE 4. Hydrolysis of aziridines by aqueous perchloric acid at 21°.

Compound	Composition of hydrolysate		10^7k	ΔH, kcal mole^{-1}	ΔS, e.u.
	S_N1, %	S_N2, %			
Aziridine	—	—	4.61	23.0±0.6	−9.4±1.0
2-Ethylaziridine	22	61	2.64	23.1±0.1	−10.0±0.5
2,2-Dimethylaziridine	80	—	21.0	24.3±0.4	−1.9±1.0
2-Ethyl-2-phenyl-aziridine	100	—	1400	23.6	1.1

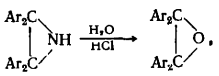
than the rates of the S_N1 reaction at the tertiary carbon of 2,2-dimethyl and 2-ethyl-2-phenylaziridine.

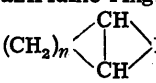
The results of the study of the steric course of hydrolysis of stereoisomeric aziridines are also ambiguous. With *cis*- and L(-)-*trans*-2,3-dimethylaziridine[302] *trans*--opening with inversion of configuration occurs, but hydration of 1,2-dimethyl-3-phenylaziridine (from *dl*-pseudoephedrine) leads to the formation of about equal quantities of *dl*-ephedrine and pseudoephedrine[311]. Finally, study of the hydrolysis of four stereoisomeric forms (*cis*, *d*, *l*, and *dl*) of 2,3-diphenylaziridine shows the predominance of *cis*-addition with retention of configuration at both asymmetric carbon atoms[312]. To a small extent *trans*-addition occurs in all the cases considered; this leads to Walden inversion at the carbon atom undergoing nucleophilic attack. The fact that racemisation does not occur in hydrolysis experiments on pure optical antipodes indicates that the configuration at the second carbon atom remains unchanged, and therefore only the C–N bond of the ring undergoes hydrolytic cleavage. Therefore, all the results mentioned indicate the presence in the hydrolysis reactions in some proportion of both (uni- and bimolecular) components of the ring-opening reaction.

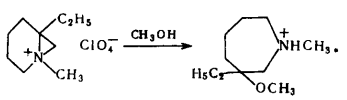
These principles are also valid for the acid alcoholysis of aziridines. Thus, alcoholysis (with methanol or ethanol) of 2,2-dimethylaziridine picrate is accompanied by preferential opening of the ring at the bond with the tertiary carbon atom, but 2-ethylaziridine picrate opens in ethanol to give a mixture of approximately equal quantities of both isomeric β-amino-ethers[235,305].



Mention should be made of an interesting hydrolytic reaction of tetra-arylaziridines, leading to derivatives of another strained three-membered heterocycle, ethylene oxide[313]:



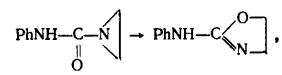
and also of the increased stability to hydrolytic cleavage of aziridine rings included in bicyclic structures of the type  , which increases further with the number *n*. Thus, trimethyleneaziridine[314], tetramethyleneaziridine[315], and pentamethyleneaziridine[316] are only hydrolysed by prolonged boiling with perchloric acid; hexamethyleneaziridine is hydrolysed by perchloric acid only at 150°;[317] and octamethyleneaziridine is not hydrolysed at all. Bicyclic aziridine derivatives with a common nitrogen atom are hydrolysed with rupture of the bridge bond and enlargement of the ring[74,318]:



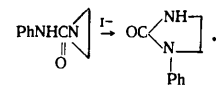
Rearrangement of aziridine derivatives occurs on heating or in the presence of catalysts. The best known catalysts are nucelophilic reagents, aluminium chloride, and acids. As a result of the reaction one C–N bond of the ring opens and a new bond is formed, usually with participation of a polar substituent in the ring.

Some rearrangements of aziridine derivatives are used for the preparation of other nitrogen heterocycles — oxazolines, imidazolines, thiazolines, etc., and also allyl amides and isocyanates.

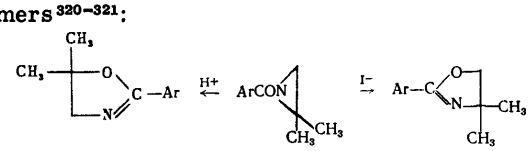
As with the aziridine ring-opening reactions by various reagents described above, the same two main ring-opening mechanisms operate in the rearrangements considered here: (1) intramolecular ionisation following rupture of the protonated ring, and (2) nucleophilic attack of the catalyst on one of the carbon atoms of the three-membered ring. The first type is most characteristic of rearrangements in the presence of acids; the second is catalysed by nucleophilic agents. Thus, in the presence of acids or simply on heating aziridinylureas rearrange by the first mechanism with the formation of corresponding derivatives of 2-oxazoline[319]



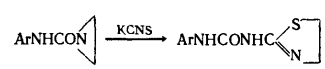
while in the presence of a large excess of a nucleophilic catalyst (for example sodium iodide) the rearrangement proceeds by the second mechanism, leading to 2-imidazoline derivatives[320]:



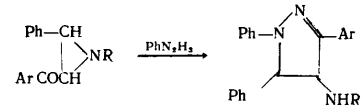
Rearrangement in the presence of a small quantity of a nucleophilic catalyst leads to a mixture of both isomerisation products[320]. Rearrangements of 1-acylaziridines, which lead to 2-oxazolines[320–324], proceed by one of the two mechanisms, depending on the catalyst, and in the case of asymmetric aziridines lead to one of the two 2-oxazoline isomers[320–321]:



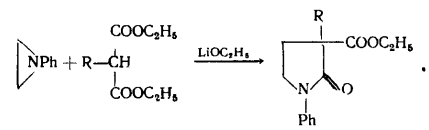
Another type of rearrangement of aziridine derivatives is that in which a molecule of the attacking reagent is included in the new ring. Examples of this mechanism include rearrangements of aziridinylureas in the presence of potassium thiocyanate, leading to 2-thiazolines[325]:



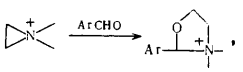
the formation of pyrazolines and pyrazoles by the reaction of β-arylaroylaziridines with phenylhydrazine[43,182,326–328]:



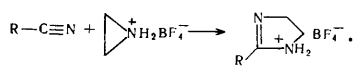
the condensation of 1-phenylaziridine with malonic ester[329]:



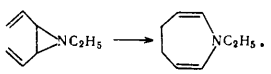
and the reaction of aziridinium salts with aromatic aldehydes[330]:



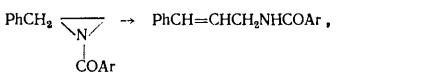
and nitriles[331]:



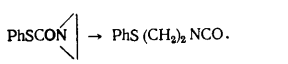
Mention should also be made of an interesting type of valence-tautomeric rearrangements of *cis*-2,3-divinyledaziridine derivatives to dihydroazepines[332]:



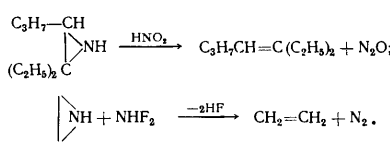
Examples of rearrangements of aziridine derivatives leading to non-cyclic compounds include the stereospecific thermal isomerisation of 1-acyl-2-alkylaziridines to the corresponding allyl amides[323,333-339]:



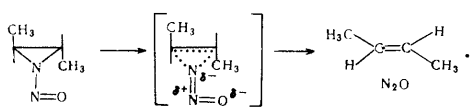
and the rearrangement of *NN*-(1-aziridinyl)-*S*-phenylthiourethane to isocyanate[340]:



Other reactions of aziridine. Deamination. Deamination of aziridine derivatives by the action of nitrosating agents[341-345] or difluoramine[346] is an interesting reaction in which both C–N bonds of the ring are simultaneously ruptured:



A study of this reaction based on the geometric isomers of 2,3-dimethylaziridine has shown that it is highly (> 90%) stereospecific[344]. The rate of deamination of aziridine derivatives is kinetically unimolecular. These facts suggest a mechanism for deamination in which simultaneous opening occurs of both C–N bonds of the ring in the *N*-nitrosoaziridine intermediate:



Reactions with natural compounds. The reaction of aziridine with cellulose, on which industrially important methods of modifying the properties of the latter are based, is of the greatest practical importance[347]. In this reaction the aziridine rings are opened by the free hydroxy-groups of the cellulose and β-aminoethylated cellulose is formed. The presence of basic amino-groups in the cellulose macromolecule does not change its mechanical properties but renders it capable of being dyed like wool with acid dyes and improves its adhesion to various fire-resisting, water-repellant and crease-resisting materials and additives. A somewhat different modification of the properties of cellulose is that produced by treatment with polyfunctional aziridine derivatives, for example, bisethyleneureas. This treatment leads to joining of the thread-like cellulose molecules by bis-(β-ureylene)alkoxy--bridges and is used industrially for the dry spinning of cellulose fibre.

The reaction of aziridine and its acyl derivatives with proteins, which is of biological interest, should also be mentioned[348]. The reactivity of proteins towards aziridine derivatives is due to the presence of acid groups in the protein molecules; the reaction probably proceeds by a mechanism in which various functional groups of the protein molecule are alkylated by protonated aziridine rings.

V. IDENTIFICATION AND QUANTITATIVE DETERMINATION OF AZIRIDINE DERIVATIVES

Numerous complex-formation[1,3,4,215] and salt-formation[6,12,21,349,350] reactions, leading to intensely coloured or poorly soluble compounds, have been proposed for the qualitative identification of aziridines. A basic disadvantage of these methods is that the reactions are common to the majority of amino-compounds, and in the presence of the latter they are of little use or entirely inapplicable. Methods based on opening of the three--membered ring, for example, the colour reaction with thiourea[351], and spectroscopy are more specific for aziridine.

The spectroscopic determination of aziridine derivatives is based on the presence in their vibrational spectra of high frequency (above 3000 cm^{-1}) C–H vibrations, due to bond strain in the three-membered rings[169-174,177,178]. The only limitation of this method is the requirement that multiple bonds and aromatic rings, which absorb in the same region, should be absent. This method is most convenient for detecting aziridine in mixtures with other aliphatic amines or in its polymerisation products.

Acidimetric titration and colorimetric methods have been described for the quantitative determination of aziridine. Recently a number of methods based on ring opening have been proposed. Obviously, these are the most specific methods.

Direct acidimetric titration is the least successful method for the quantitative determination of aziridine, because of the considerable number of side-reactions; these include polymerisation, hydrolysis, and nucleophilic ring opening by acids[20,199,202-204]. Colorimetric methods based on double decomposition with the potassium salt of 1,2-naphthoquinone-4-sulphonic acid are also not specific for aziridine[351,352]. Extraction with chloroform of the dye formed in aqueous solution has been proposed to increase the sensitivity of this method.

As with qualitative identification, the most specific and reliable quantitative methods are based on reactions in which the aziridine ring is opened by various nucleophilic agents. These methods include the extremely sensitive colorimetric determination of the product of the reaction of aziridine with γ(-4-nitrobenzyl)pyridine, proposed for the determination of very small quantities of aziridine in water and in air[353]. Reactions of this group suffer from one general disadvantage: they have a very low velocity,

which is characteristic of non-ionic reactions. Because of this the methods are generally used indirectly. Attempts to improve them involve a search for effective nucleophilic agents that would give the maximum reduction in the time of reaction with aziridine.

The most widely used method of this group, the thiosulphate method[354-357] and its latest modification in which thiocyanate is used[358], are based on the determination of alkali formed as a result of rupture of the aziridine ring by $S_2O_3^{2-}$ or CNS^- ions in an acidified solution. The second method of this group is a combination of the acidimetric method and ring opening by acid. The sample containing aziridine is boiled with an excess of acid, which is then determined by back titration[215]. The latest modification of this method comprises direct titration of aziridine derivatives with a solution of perchloric acid in acetic acid or dioxan in the presence of an excess of quaternary ammonium iodide[359]. The method is based on the rapid opening of the aziridine ring by hydriodic acid immediately it is formed (by displacement with perchloric acid from the quaternary ammonium salt). Verification of the results obtained by means of the thiocyanate method shows that direct titration is of sufficiently high accuracy.

VI. ACTION ON LIVING ORGANISMS

Aziridine and its derivatives surpass all known chemical compounds in their biological activity and in their many-sided action on living organisms (toxicity, mutagenesis, cytostatic properties). Since their action is very similar to that of penetrating radiation, they have been called radiomimetic compounds. The biological effect of aziridine derivatives is widely used in various fields of science and technology and therefore deserves special consideration.

Toxicity. Aziridine is extremely poisonous[360-366]. A single oral dose of 15 mg per kg of body weight is lethal. Death usually occurs in 1 to 24 hours as a result of respiratory paralysis[361]. It has been noted that in aziridine poisoning death can occur even 10 days after a symptomless period as a result of a combination of pulmonary and renal lesions with leukopenia[365-367].

The danger of poisoning by aziridine vapour is aggravated by the great similarity of its odour to that of ammonia, and also by the absence of symptoms during exposure[368]. The first signs of aziridine poisoning only appear after 2–8 h in the form of nausea and vomiting, and inflammation and oedema of the mucous membrane of the mouth, throat, and eyes[368,369]. A single exposure for 30–60 minutes to a concentration of 250 parts per million in air is dangerous to life[369]. Hydration, antihistamines, steroids, antibiotics, expectorants, and enzyme therapy are used in the treatment of aziridine poisoning[370]. It has been noted that, when suitable safety measures are taken, work with aziridine in the laboratory can be carried on for a long time without danger to health[368]. An ordinary gas mask provides individual protection against aziridine vapour.

Aziridine is readily absorbed by the skin and produces blisters and rashes that are difficult to heal[371]. Prolonged action of aziridine on the unprotected skin produces symptoms of systemic poisoning.

Mutagenic activity. Aziridine and its derivatives are the most powerful chemical mutagens. The mechanism of chemical mutagenesis by aziridine derivatives involves attack by the aziridine molecule on the pyrimidine precursors of deoxyribonucleic acid[372,373]. Compared with irradiation by ultraviolet light and X-rays, aziridine derivatives produce the maximum number of mutations per thousand surviving spores[374]. The combined effect of irradiation and the action of aziridine derivatives has a much greater mutagenic effect than each of these separately[375]. Aziridine and its derivatives are widely used in agricultural and industrial selection to increase the productivity of agricultural crops and for the selection and growth of strains of antibiotic producers.

Cytostatic activity. The discovery that triethylenemelamine, phosphoraziridates, and certain other aziridine derivatives can prevent the reproduction (mitosis) of plant and animal cells has prompted an extensive search for similar compounds amongst other aziridine derivatives. The exceptional interest in these compounds is due to the wide use of their cytostatic activity in the treatment of various forms of neoplastic disease, such as cancer, sarcoma, and malignant blood diseases.

VII. MAIN TECHNICAL USES

It has been noted above that the unique chemical, physicochemical, and biological properties of aziridine find considerable use in various branches of science and technology. We shall consider some of them briefly.

Judging from the number of publications, aziridine and its derivatives are most widely used in the textile and paper industries. Aziridines, which are fairly powerful alkylating agents (as a result of the opening of the three-membered ring), readily react with most compounds that form natural and synthetic fibres and paper; since amino-groups are introduced into the compounds, their properties are modified. Cellulose, acetylcellulose, viscose, and other cotton fibres acquire the capacity to take acid dyes in the same way as wool[376]. This also holds for most synthetic fibres; these include polyacrylic[377], vinylidene cyanide[378] and polyvinyl-alcohol[379] fibres. Polyalkene fibres, which have the best mechanical properties but contain no reactive groups in the molecule, must be partially oxidised[380] or subjected to γ-irradiation[381] before treatment with aziridine[381]. Treatment of synthetic and natural fibres with aziridine derivatives greatly increases their water-resistance[382,383]. Wool and other protein fibres acquire resistance to laundering[384], do not shrink, and do not break off after they have been treated with bisalkyleneureas, or other aziridine derivatives containing at least two aziridine rings in the molecule (because of the formation of cross-linking bonds in the keratin). Synthetic fibres and fabrics made from them do not accumulate electric charges when they have been treated with aqueous solutions of polyaziridine and some aziridine derivatives[365].

The addition of 0.3–0.6% of aziridine or polyaziridine in the process of paper making accelerates the coagulation of the paper mass and increases the productivity of the paper-making machines[386]; it also permits the use of raw material with low drainage properties, activates the cellulose fibres, increasing their adhesion to fillers[387], and increases (by about 60%) the mechanical strength of the paper under wet conditions and also its ability to fix dyes and pigments[368].

Some aziridine and polyaziridine derivatives are used in photography to strengthen the emulsion gelatin[389] and to fix a colour image on it[390], to sensitise photographic materials[391], and as developers of colour photographs[392].

Some cytostatically active aziridine derivatives find a very interesting use in the control of mosquitos, flies, and other blood-sucking insects[393,394]. The active compound (usually triaziridinylphosphine oxide or sulphide) is added in the proportion of 0.5% to the insect food (a corn bait); when the individuals that have eaten it are distributed amongst the natural populations, the latter are exterminated in about three generations[395].

The use of aziridine and a number of its derivatives in rocket engineering should also be mentioned. The high heat of formation, associated with the closure of the three-membered ring, the tendency to ignite spontaneously with most oxidising agents, and also the low melting point and relatively high density make aziridine[396,397] and 1-aminoaziridine[398] attractive combustible components of highly effective fuels for liquid rocket motors. Aziridine derivatives containing several aziridine groups in the molecule (for example, triaziridinylphosphine oxide and sulphide and triethylenemelamine) are used for hardening the composition of a mixed solid rocket fuel based on synthetic polymers containing terminal acid groups[399,400]. The fuels thus obtained have better physicomechanical characteristics compared with similar compositions hardened by epoxides[399].

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ADVANCES IN THE CHEMISTRY OF IMIDAZOLE

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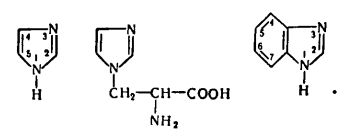
I. INTRODUCTION

In recent times progress in the chemistry of certain classes of organic compounds has been closely related to advances in molecular biology. A striking example of this is the chemistry of imidazole (I) and its derivatives. Numerous natural compounds (enzymes, nucleic acids, alkaloids, etc.), which include in their composition the imidazole group, have been known for a long time. A new antibiotic, azomycin (2-nitroimidazole)[1-3] and a new amino-acid, isohistidine (II)[4], are further additions to this series of compounds.



(I) (II) (III)

At the beginning of the 1950's it was shown that purines are not the only condensed imidazole system which plays a role in vital processes. It was found that the structure of vitamin B_{12} incorporates a 5,6-dimethylbenzimidazole fragment[5]. This finding greatly stimulated the development of the chemistry of imidazoles condensed with aromatic rings, and in the first place of benzimidazole (III).

The advances in the elucidation of the role of the imidazole group of enzymes and nucleic acids in the chemistry of the most important living processes has been particularly remarkable[6,7]. All these discoveries naturally enough also required a considerable effort in research on the chemistry of imidazole. In terms of the volume and importance of the studies on imidazole and its derivatives the last decade may be compared to the entire preceding period. In this connection it is necessary to sum up all this work, particularly as the latest reviews on the chemistry of imidazole[8] and benzimidazole[9] cover the literature only up to 1951. In a number of monographs on the chemistry of heterocyclic compounds[10-15] the chemistry of imidazole is dealt with in a very brief and incomplete manner.

The present review covers the literature on the chemistry of imidazole and the most important imidazole derivatives condensed with aromatic rings from 1952 to 1963

(partly also 1964) inclusive. In view of their unusual properties, it is desirable to consider separately condensed imidazole systems consisting of two and more heterocyclic rings (imidazopyridines, purines, etc.)[16]. The extensive biochemical and pharmacological data on imidazoles, which themselves can be and already have been[6] the subject of a review, will be used only partially in dealing with the main problem — the exposition of the present state of the chemistry of imidazole.

II. SYNTHESIS OF IMIDAZOLES

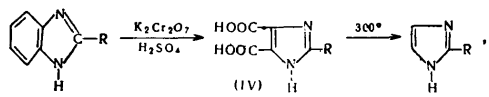
A. NON-CONDENSED IMIDAZOLES

The classical synthesis of imidazoles by the method of Debus and Radziszewski (reaction of α-diketones with ammonia and aldehyde) has a number of disadvantages[8]. In the 1930's two important modifications of this method were proposed: Weidenhagen's method, consisting in the reaction of α-hydroxy-ketones with ammonia and an aldehyde in the presence of copper acetate (sometimes copper citrate or sulphate is used) and Davidson's method, consisting in the reaction of α-diketones with an aldehyde and ammonium acetate in glacial acetic acid. Both these modifications have not lost their value even now. They are widely used for the preparation of a wide variety of mono-, di-, and tri-*C*-substituted (substituent — alkyl, cycloalkyl, aralkyl, aryl, or a heterocyclic residue) derivatives of imidazole[17-25] and 2-imidazolyl ketones[26].

One of the most important achievements in the chemistry of imidazole in recent years is the formamide synthesis of imidazoles proposed by Bredereck and Theilig[27]. It consists in the reaction between α-diketones or α-substituted ketones (substituents — halogeno-, hydroxy-, amino-, or isonitroso-groups) and formamide. As a rule high yields and simplicity are the main advantages of this method. However, it has limited applicability for the preparation of 2-substituted imidazoles, since it is then necessary to replace formamide by the amides of more complex acid and this reaction has so far been relatively little investigated[28,29]. Although a review of formamide syntheses was published in 1959[30], we shall consider this question briefly, since a number of new papers have been published since then.

1. Imidazole and Its Simplest 2-Alkyl(Aryl) Derivatives

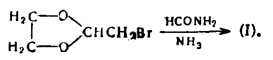
A widely used synthesis of imidazole is from imidazole-4,5-dicarboxylic acid (IV) obtained by the oxidation of benzimidazole with chromic acid mixture[31]. 2-Methyl- and 2-ethyl-imidazoles are synthesised similarly[32-34]:



where R = H, CH_3, C_2H_5.

It is interesting that *N*-substituted benzimidazole derivatives cannot be converted in this way to the corresponding di-acid (IV).[31] Imidazole-4,5-dicarboxylic acid is also readily formed on hydrolysis[35] of its diethyl ester. In their synthesis of 2-cycloalkylimidazoles, Schubert and Ladish[37] also started from the corresponding di-acids obtained by Maquenne's method[8].

A new and probably the most economical synthesis of imidazole itself is the reaction between the glycol acetal of α-bromoacetaldehyde and formamide[38]:

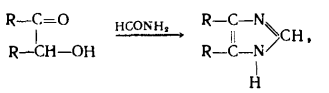


The preparation of imidazole and its 2-alkyl(aryl) derivatives by the reaction of ethylenediamine with the corresponding alcohol, aldehyde, or acid at a high temperature in the presence of Pt/Al_2O_3 has been patented[39,40]. The yields of products are very high, but the method is experimentally very complex. 2-Benzyl- and 2-α-naphthylmethyl-imidazoles are comparatively readily obtained from ethylenediamine and phenyl- or α-naphthyl-acetic acids[41].

Reductive aminolysis of glyoxal, methylglyoxal, and acetoin with ammonia or hydroxylamine leads to the formation of imidazole only in the case of glyoxal[42].

2. *C*-Alkyl-, *C*-Aralkyl-, and *C*-Aryl-imidazoles

a. From α-hydroxy-ketones. 4,5-Disubstituted imidazoles can be obtained in excellent yield by boiling α-hydroxy-ketones with formamide for 2–4 h[24,27]:

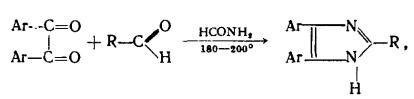


where R = alkyl, aryl, α-furyl, 4,5-octamethylene, etc. Highly branched α-hydroxy-ketones (hexamethylacetoin, tetrabenzylacetoin) do not form imidazole on heating with formamide.

A small amount of 4,5-disubstituted oxazole forms as a side-product. If conditions in which the imidazole ring is formed preferentially (large excess of formamide, t = = 180–200°) are not maintained, the formation of oxazole may begin to predominate. This situation is also favoured by the use of sulphuric acid as a condensing medium[43].

b. From carbohydrates. This pathway has been used in recent years mainly for the preparation of 4-hydroxymethylimidazole used in the synthesis of histamine[44,45]. An improved method of synthesis of 4-methylimidazole from glucose has been described[46].

c. From α-diketones. On reaction with aldehydes and formamide, α-diketones give 2,4,5-trisubstituted imidazoles in yields of 27–67%:[28]

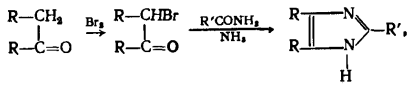


where Ar = C_6H_5, *p*-BrC_6H_4, *p*-$CH_3OC_6H_4$, *o*-ClC_6H_4; R = H, C_6H_5, 3,4-$Cl_2C_6H_3$.

On boiling with formamide (190°, 4 h) di-(2-furyl)-ethane-1,2-dione gives 2,4,5-trifurylimidazole; on the other hand, if a mixture of formamide and formic acid is used, 4,5-difurylimidazole is formed[47].

d. From α-halogeno-ketones. When α-halogeno-derivatives of aliphatic and aliphatic–aromatic ketones are boiled in formamide, 4,5-disubstituted imidazoles are formed[22,27]. 4-Phenylimidazole can be

obtained by this reaction from phenylacyl bromide in 90% yield. It is very convenient to brominate the ketone with an equimolar amount of bromine in formamide[48] or acetamide[29] and then, without isolating the α-bromo--derivatives, pass ammonia into the mixture heated to 180°:

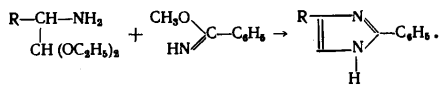


where R′ = H, CH_3.

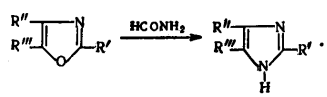
The preparation of 4,5-disubstituted imidazoles from 1-chloro-1,2-epoxides and formamide described by Durgaryan[49] may be regarded as a special case of this reaction. As before, imidazoles are also synthesised from α-halogeno-ketones by Kunckell's amidine method[20,50].

e. From α-amino-ketones and α-iso-nitroso-ketones. α-Amino-ketones and their α-acyl derivatives form the corresponding imidazoles in good yields on reaction with formamide[27,51] or ammonium acetate in acetic acid[51,52]. When benzil mono-oxime reacts with formamide in the presence of sodium hydrosulphite, 4,5-diphenylimidazole is formed in 71% yield[27]. The reaction of benzil mono-oxime with benzaldehyde is more unusual[53], resulting in an almost quantitative yield of 2,4,5-triphenylimidazole instead of the expected oxazole.

2-Phenylimidazole and its 4(5)-alkyl derivatives may be obtained[54] by the condensation of the acetals of α-amino--aldehydes with benzimidates in aqueous alcohol at pH 7:

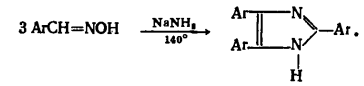


f. From oxazoles. It follows from what has been said above that formamide syntheses of imidazoles are frequently complicated by the formation of oxazoles. In order to find the optimum conditions for the formation of imidazoles from α-substituted ketones, Theilig studied the reaction of oxazoles with formamide[55]. After boiling for 3–6 h with formamide, most oxazoles were converted into the corresponding imidazoles in satisfactory yields:

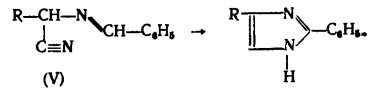


Oxazoles containing aliphatic radicals (C_3H_7, C_4H_9) in positions 2 and 5 were an exception. Some of these "difficult" oxazoles are converted into the imidazoles on reaction with formamide and ammonia in an autoclave at 200–210°.[56] Aromatic substituents, in particular in position 4 of the oxazole ring, facilitate the imidazole synthesis, probably by lowering the electron density at the oxygen atom[57,58]. Hence it follows that halogenoalkylated oxazoles should form imidazole even more readily; this is in fact found to be the case[57]. Benzimidazole cannot be obtained from benzoxazole in this way, although it would appear that a condensed benzene ring should also facilitate this reaction[57]. The mechanism of the formation of the imidazole ring from oxazoles and formamide has been discussed by Theilig[55]. A case is also known of the opposite conversion — of the imidazole ring into the oxazole ring[59].

g. Other methods. 2,4,5-Triarylimidazoles are formed in yields of 72–77% when aldoximes are heated with sodium amide in absolute xylene[60]:

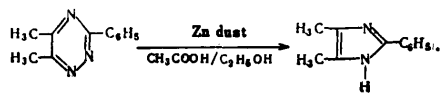


On prolonged storage or on distillation, benzylideneamino--derivatives (V) are converted into 2-phenyl- or 2,4(5)-diphenyl-imidazoles[61]:



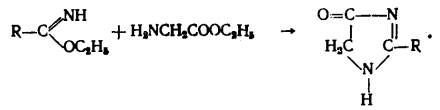
(V)

Metze and Scherowsky[62] observed an interesting case of contraction of the 1,2,4-triazine ring to the imidazole ring. They suggested the following mechanism for this reaction[62]:



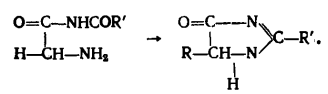
3. Hydroxyimidazoles

Relatively little work has been done on 4(5)-imidazolones. The principal method for their preparation is still the reaction of imidates with the ethyl ester of glycine:



Finger's classical work in this field[8] was checked[63,64] and a number of improvements have been made in the method of preparation of imidazolones. The synthesis of imidazolones from imidates is described in greater detail in the review of Roger and Neilson[65].

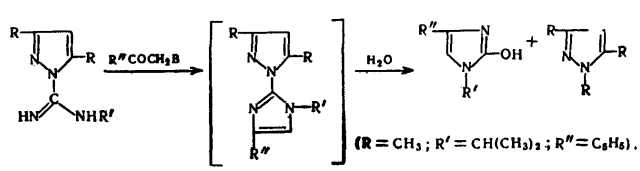
A new method for the synthesis of 4(5)-imidazolones consists in the spontaneous cyclisation of *N*-acylated amides of α-amino-acids[66,67]:



The substituent R in this reaction is usually an electrophilic group, such as CN, COOR, COR, etc.

2-Hydroxyimidazole and its 4(5)-substituted derivatives can be conveniently obtained by the action of potassium cyanate on solutions of amino-aldehydes made by the reduction of α-amino-acids with sodium amalgam[68].

Recently 2-hydroxy-1-isopropyl-4-phenylimidazole was synthesised in 51% yield by a fundamentally different procedure[69]:



(R = CH_3; R′ = $CH(CH_3)_2$; R″ = C_6H_5).

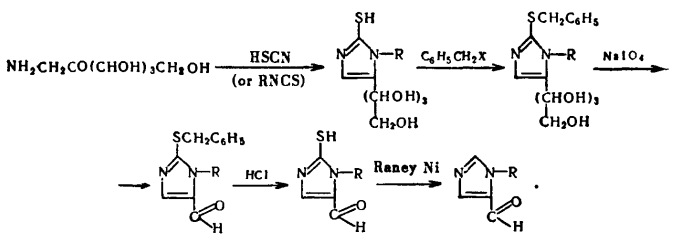
Some problems concerning the synthesis of imidazolones are also discussed by Roger et al. [70] and Wieland and Biener [71].

4. Mercaptoimidazoles

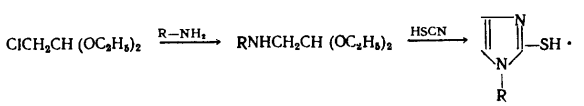
2-Mercaptoimidazoles are biochemically important as antithyroid agents, and Marckwald's synthesis of imidazoles [8] [reaction of α-amino-carbonyl compounds with thiocyanic acid or alkyl(aryl) isothiocyanates] is second in importance only to the method of Debus and Radziszewski, since sulphur can be readily removed from the resulting 2-mercaptoimidazoles with nitric acid, ferric chloride, hydrogen peroxide, or Raney nickel.

The principal problem in the preparation of 2-mercaptoimidazoles remains the synthesis of the initial α-amino--aldehydes and α-amino-ketones. The reduction of α-amino-acids with sodium amalgam [72-74] is in this case preferable to phthalimide methods [75,76] or the Dakin–West reaction [77-79], since it does not require the preliminary isolation of the α-amino-aldehyde from the reaction mixture and because the initial α-amino-acids are available.

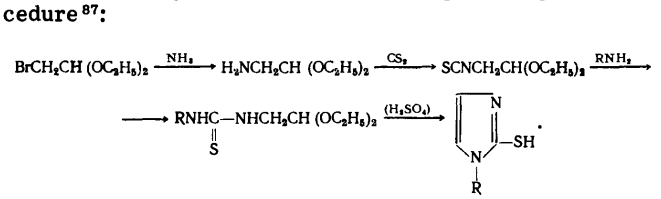
D-Glucosamine [80-83] or 1-alkylamino-1-deoxy-*D*--fructose [84] can serve as a source of 2-mercapto--4-(arabotetrahydroxybutyl)imidazoles which can be converted into 4-formylimidazoles:



N-Alkyl(aralkyl)-2-mercaptoimidazoles can be conveniently synthesised starting with *N*-substituted amino--acetals [85,86]:



A number of 2-mercaptoimidazoles containing alkyl, aralkyl, aryl, and 2-thiazolyl groups in position 1 have been obtained by a somewhat more complicated procedure [87]:

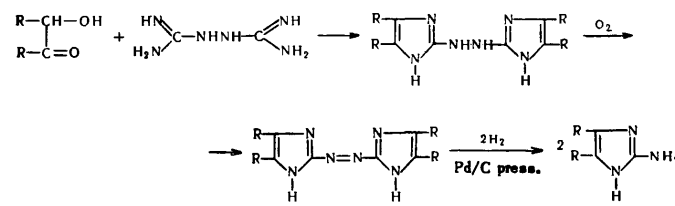


The condensation of the hydrochlorides of α-amino--ketones with potassium thiocyanate is best carried out in non-aqueous solvents (absolute alcohol, glacial acetate acid, etc.), since in aqueous media a certain amount of a pyrazine derivative is also formed as a result of the hydrolysis of the α-amino-ketones [88].

The methods of preparation of 4,5-dialkyl(diaryl)- and 1,4,5-triaryl(trialkyl)-imidazoles from α-hydroxy-ketones and thiourea or its *N*-substituted derivatives has been improved [89].

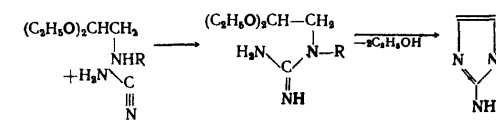
5. Aminoimidazoles

2-Aminoimidazoles have been little investigated so far because of the lack of convenient methods for their synthesis. The classical procedure for the synthesis of 2-aminoimidazoles consists in the reduction of azo-imidazoles obtained by coupling diazonium salts with imidazoles containing a free NH group [8]. However, not only are the yields low but the method is not always applicable [90]. A new promising modification of this method is via the synthesis and reduction of 2,2′-azo-imidazoles [91]:



where R = C_6H_5, $CH_3OC_6H_4$, β-$C_{10}H_7$, α-pyridyl. The yields of 2-amino imidazoles reach 89.5% in this case.

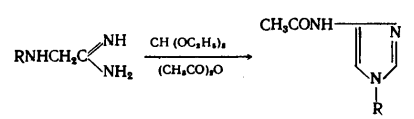
2-Amino-4,5-diarylimidazoles can also be obtained by the benzidine-like rearrangement of 2-phenylhydrazino-imidazoles [92] or by the reduction of the relatively readily available derivatives of 2-benzylidenehydrazinoimidazoles [93]. The most convenient method for the preparation of 2-aminoimidazole and its 1-alkyl derivatives is by the reaction of cyanamide with α-amino-acetals [94]:



The reaction of D-glucosamine with cyanamide gives 2-amino-4-(arabotetrahydroxybutyl)imidazole [95,96]. The preparation of 2-guanidino-4(5)-phenylimidazoles from phenylacylamines and cyanoguanidines is based on a similar reaction [97].

6. 4(5)-Aminoimidazoles and 4(5)-Aminoimidazole--5(4)-carboxamides

Two new methods for the preparation of 4(5)-amino-imidazoles have been proposed recently. In one of them the starting materials are the hydrochlorides of benzyl-oxycarbonyl or tosyl derivatives of aminoacetamidine and orthoformic ester [98]:

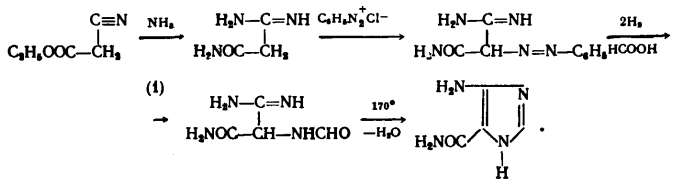


where R = *p*-$CH_3C_6H_4SO_2$ (a) and R = $C_6H_5CH_2OCO$ (b).

In the other method dinitriles RN(CN)CH(CN)R′ are cyclised into 4(5)-amino-2-bromoimidazoles by treatment with anhydrous hydrogen bromide [99].

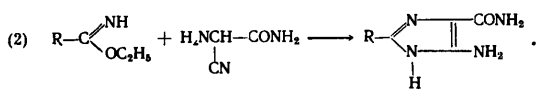
4(5)-Aminoimidazole-5(4)-carboxamides are of exceptional interest as the biosynthetic precursors of

purines [100]. At present several methods are known for the preparation of these compounds:

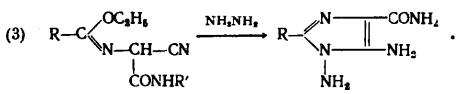


This method, proposed for the first time by Shaw and Woolley [101], is most convenient, after certain modifications [102-104], for the synthesis of large amounts of 4(5)-aminoimidazole-5(4)-carboxamides under laboratory conditions.

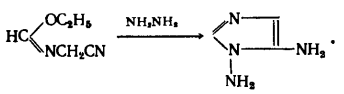
The reaction of amidines [105] or imino-esters [106] with aminocyanoacetamide proceeds as follows:



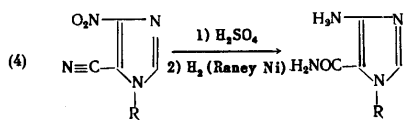
The reaction between *N*-(carbamoylcyanomethyl)imidates and hydrazine, phenylhydrazine, or 1,1-dimethylhydrazine yields the corresponding 1,5-diamino-4-carbamoylimidazoles [107,108]:



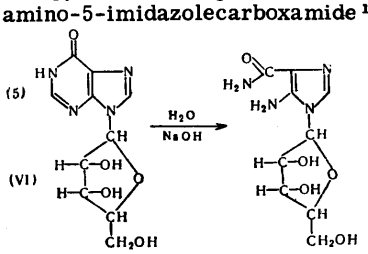
The parent compound of the series, 1,5-diaminoimidazole, is formed from ethyl *N*-cyanomethylformimidate and hydrazine [107]†:



Hydrazines not containing a free NH group, for example 1,2-dimethylhydrazine, do not give imidazoles in this reaction but 1,2,4-triazines. If a primary amine is used instead of hydrazine, it is possible to obtain 1-alkyl-(glucosyl)-5-amino-4-carboxamidoimidazoles [110-113]:



In the alkaline hydrolysis of certain purines, for example (VI), the pyrimidine ring opens forming the corresponding 4-amino-5-imidazolecarboxamide [104]:



In an acid medium the carbohydrate residue also hydrolyses.

† 1-Amino-2-mercaptoimidazoles have been described recently [109].

B. BENZIMIDAZOLES

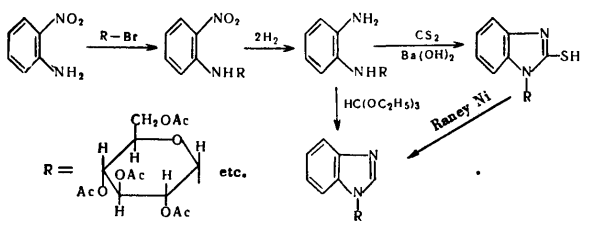
The principal method for the preparation of benzimidazoles is still condensation of *o*-arylenediamines with carboxylic acids and their derivatives. Attempts to find new ways of synthesising benzimidazoles, such as thermal decomposition of 1,5-diaryltetrazoles and 1,2,4-oxadiazol--5-ones [114-119] or the rearrangement of *N*-aryl-*N*-hydroxyamidines [120] are not of any preparative importance.

At the same time the classical synthesis of benzimidazoles from *o*-arylenediamines has been significantly modified. The method involving the ring closure of the imidazole ring of benzimidazole using directly the corresponding *o*-nitroanilines has been further developed, the reduction and cyclisation stages being combined into one [121-123]. Phillips' method for the synthesis of 2-arylbenzimidazoles has been improved [124-130], and many new modifications have been introduced into the reaction of *o*-arylenediamines with aldehydes [131-134].

1. Benzimidazoles without a Substituent in Position 2

The formation of benzimidazole from *o*-phenylenediamine and formic acid proceeds with exceptional ease: close to physiological conditions (18°, pH 0.5) the yield of benzimidazole after five days is 83%. [135] At 100–110° the time required for this yield is reduced to 2 h. Various benzimidazoles substituted in the benzene ring (substituents — alkyl, halogeno-, hydroxy-, alkoxy-, amino-, and nitro-groups, etc.) can be obtained just as readily by means of this reaction.

In connection with the interest attaching to vitamin B_{12}, much work has been done on the preparation of 5,6-dimethylbenzimidazole [121,136-141] and *N*-glycosidobenzimidazole [142-148]; particular attention has been devoted to 5,6-dichloro- and 5,6-dimethyl-1-glycosidobenzimidazoles [149], in view of their high physiological activity. 1-Glycosidobenzimidazoles are synthesised starting with the corresponding *o*-nitroaniline and acetylated glycosyl bromide:



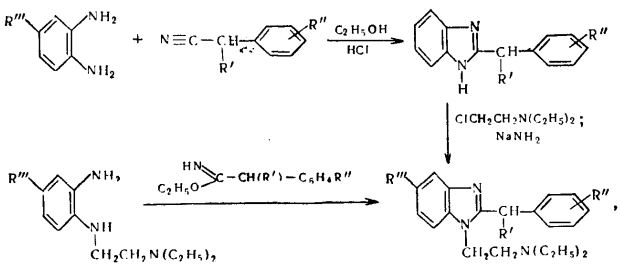
The condensation of *N*-substituted *o*-phenylenediamine is achieved with the aid of orthoformic ester, ethyl formate, or ethyl formimidate. Cyclisation under mild conditions can also be carried out by reaction with carbon disulphide in the presence of barium hydroxide [144,146]. The mercapto--group is subsequently eliminated with Raney nickel. A large number of *N*-arylbenzimidazoles have been obtained from *o*-aminodiphenylamine derivatives and formic acid.

2. 2-Alkyl(Aralkyl)benzimidazoles

The reaction of *o*-phenylenediamine and its 4-methyl-, chloro-, amino-, and alkoxy-derivatives with a number of aliphatic, aliphatic–aromatic, and aromatic acids in the presence of hydrochloric acid has been investigated [124-127].

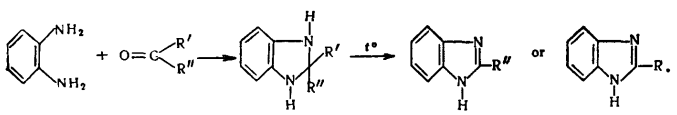
The yield of the 2-substituted benzimidazole depends on the nature of the diamine and carboxylic acid and on the concentration of hydrochloric acid. For example, it proved possible to obtain 2-benzyl- and 2-β-phenylethylbenzimidazoles in yields up to 88–99%.

Many 2-benzylbenzimidazoles have been synthesised according to the following scheme [151–154]:



where R′ = H, $CH_2CH_2N(C_2H_5)_2$, $CONH_2$; R″ = H, Cl, CH_3, AlkO; R‴ = H, NO_2. Many of these substances are muscle relaxants and are effective analgesics.

The reaction of *o*-phenylenediamine (VII) with aliphatic or aliphatic–aromatic ketones yields imidazolines which on thermal decomposition lose a hydrocarbon molecule (R′H or R″H) and are converted into 2-substituted benzimidazoles [155–157]:



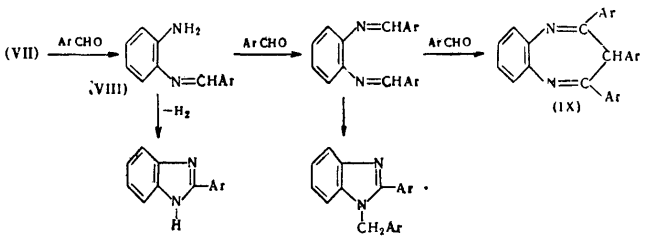
(VII)

The primary product of the reaction of *o*-phenylenediamine with benzophenone and its derivatives is not imidazoline but a Schiff's base [156] which on prolonged heating at 250–280° is converted into 2-arylbenzimidazole.

3. Benzimidazoles with Aryl or Heterocyclic Substituents in Position 2

Many new successful methods have been proposed for the synthesis of 2-acrylbenzimidazoles [124–133,158–162]. For example, 2-phenylbenzimidazole can be obtained in 76–95% yields from *o*-phenylenediamine and benzoic acid [124–127,129] or its derivatives: esters [129], nitrile [129,160], amide [129,161], and imidates [65,158,159]. The reaction is usually carried out by fusing together the components at 180–250° or by heating in a high-boiling solvent in the presence of condensing agents (hydrochloric acid, polyphosphoric acid, and others). We believe that the simplest and most convenient procedure is that of Porai-Koshits and coworkers in which equimolar amounts of *p*-phenylenediamine and benzoic acid are heated in a sealed tube at 180° in the presence of 25% hydrochloric acid. After heating for 40 min the yield of 2-phenylbenzimidazole is 95%. In the absence of hydrochloric acid the yield falls to 65% and when halogenobenzoic acids are used it is only 49% or less [162–163].

In the reaction of *o*-phenylenediamine with an equimolar amount of an aromatic or heterocyclic aldehyde a monoanil (VIII) is formed in the first stage and in the presence of oxidising agents can then yield a 2-substituted benzimidazole. The most successful oxidising agent, which at the same time serves as a solvent, proved to be nitrobenzene [131–133]. Sometimes (with 9-formylanthracene [164] and furfural [165]) the anil (VIII) is spontaneously oxidised by atmospheric oxygen to 2-substituted benzimidazole:



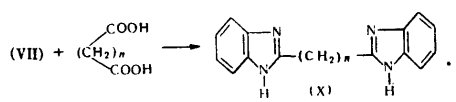
Depending on the conditions and on the nature of the reactants, in the reaction of *o*-arylenediamines with two and more moles of an aldehyde there is preferential formation of the corresponding 1-benzyl-2-arylbenzimidazole, 2-arylbenzimidazole, or, most often, their mixture with a small amount of 2,3,4-triaryldiazepine (IX). There is a review on the preparation of benzimidazoles from *o*-phenylenediamines and aromatic aldehydes [134].

None of these methods is universal but together they make it possible to synthesise any benzimidazole derivative. Thus in the synthesis of benzimidazoles with heterocyclic substituents in position 2 (pyridyl, quinolyl, furyl, thienyl, pyrrolyl, thiazolyl, etc.) best results are obtained by using aldehydes in the presence of oxidising agents, imidates [165], or acid amides [166].

Weidenhagen's classical method has been widely used in the synthesis of a large number of new 2-arylbenzimidazoles and their *N*-alkyl(aryl) derivatives [150,167]. The synthesis of 2-arylbenzimidazoles by the reaction of *o*-phenylenediamine with anil cyanides, ω-cyanoacetophenone, nitrones [168], and αβ-unsaturated compounds of the type ArCH=CHCOR [169] while not of preparative importance is of theoretical interest. 2-Phenylbenzimidazole forms in 40% yield in the pyrolysis of *N*-benzyl-*o*-nitroaniline in the presence of iron oxalate [123].

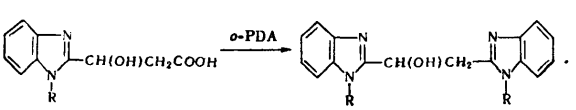
4. Bis(2-benzimidazolyl)alkanes and Related Compounds

In the reaction of *o*-phenylenediamine with dicarboxylic acids using Phillips' procedure [130,170–172] or at 190° [173] the corresponding bis(2-benzimidazolyl)alkanes (X) are formed:

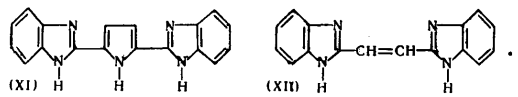


The synthesis of compound (X) with $n = 0$ and 1 can be achieved by using the diamide of oxalic or malonic acid [161,174]. For large values of n (8–10), the synthesis of compound (X) becomes difficult. Best results are then obtained when polyphosphoric or concentrated sulphuric acids are used as the catalysts [130].

Equimolar amounts of *o*-phenylenediamine (PDA) and malic acid give a β-hydroxy acid which on boiling with *o*-phenylenediamine gives a bis-derivative [171]:



The reaction between saccharic acid and *o*-phenylenediamine yields 1,4-bis(2-benzimidazolyl)-2,2,3,4-tetrahydroxybutane which can be converted to αα-bis(2-benzimidazolyl)pyrrole (XI) [175]:



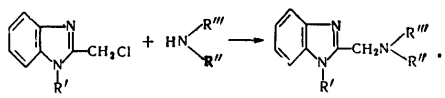
(XI) (XII)

The furan analogue of compound (XI) has also been described [176].

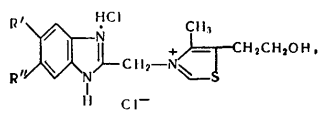
Various derivatives of 1,2-bis(2-benzimidazolyl)ethylene (XII) have been synthesised [177-179]. In the oxidation of bis(2-benzimidazolyl)methane or tetra(2-benzimidazolyl)-ethane Arnold obtained tetra(2-benzimidazolyl)ethylene, which is a powerful yellow chromophore [180].

5. 2-Aminoalkylbenzimidazoles and Amino-Acids of the Benzimidazole Series

2-Aminoalkylbenzimidazoles of various structures are readily obtained in the reaction between 2-chloromethylbenzimidazoles and a wide variety of primary and secondary amines [181-185]:



With tertiary amines quaternary ammonium salts are obtained. In particular, benzimidazolylmethyl analogues of thiamine have been prepared [186]:



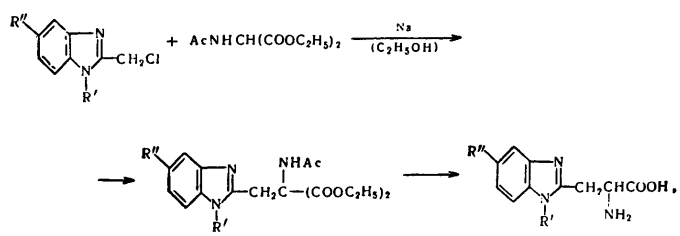
where R′ = H, CH_3; R″ = H, CH_3, Cl, CH_3O, $COOC_2H_5$.

Primary 2-aminoalkylbenzimidazoles can also be obtained by the reduction of nitriles [187], Hofmann degradation of amides, or by the Gabriel synthesis [188]. Until recently it was believed that the reaction between α-amino-acids and *o*-phenylenediamine does not give benzimidazole derivatives. However, it has been shown in a recent study [189] that, when the duration of heating is greatly prolonged, 2-aminoalkylbenzimidazoles can be obtained in satisfactory yield by this procedure. The reactivity of α-amino-acids in this reaction falls in the series glycine, alanine, α-aminoisobutyric acid. β-Amino-acids enter into this reaction much more readily.

Methods have been developed for the synthesis of 2-aminoalkylbenzimidazoles from *o*-phenylenediamines and peptides [190], benzyloxycarbonyl and *p*-tosyl derivatives of amino-acids, and their imino-ethers [191,192]. The reaction of *o*-phenylenediamine with peptides has been suggested for the identification of *C*-terminal amino-acid residues in peptides.

Attempts are being made to synthesise biologically active amino-acids containing a 2-benzimidazole residue.

Usually the synthesis is begun with 2-chloromethylbenzimidazoles and ethyl acetamidomalonate [187,193-196]:



where R′ = H, Alk, Ar; R″ = H, NO_2, CH_3, $N(CH_2CH_2Cl)_2$. In those cases where the method is inapplicable, a different procedure is followed, for example via the corresponding hydantoin [189]. The methods for the preparation of *N*-(2-benzimidazolylmethyl)amino-acids have been discussed [197].

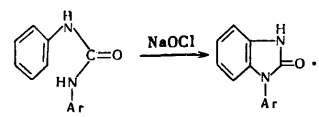
6. 2-Polyhydroxyalkylbenzimidazoles

The syntheses of 2-polyhydroxyalkylbenzimidazoles have been described in the monograph of Zhdanov and Dorofeenko [198].

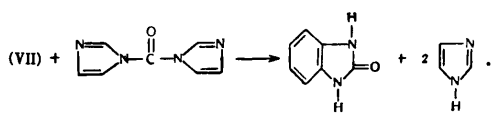
7. 2-Hydroxy- and 2-Mercapto-Benzimidazoles

2-Hydroxybenzimidazoles are readily formed from *o*-phenylenediamines and urea or phosgene [199-202]. In the first case the reaction components are fused together at 140–180° and in the second phosgene is bubbled through an acid aqueous solution of the diamine. Similarly 2-mercaptobenzimidazoles are formed from thiourea and phosgene [203-208].

A new method for the preparation of *N*-arylbenzimidazol-2-ones consists of the oxidation of *NN′*-diarylurea with sodium hypochlorite [209,210]:



Benzimidazolones are also formed in high yields in the reaction of *o*-phenylenediamines with *NN′*-carbonyldiimidazole [211]:



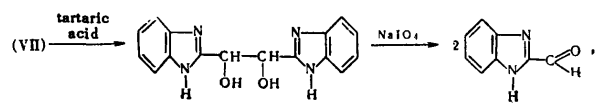
These compounds have been shown by means of electronic and vibrational absorption spectra to have the benzimidazolone and not the hydroxybenzimidazole structure [212,213].

8. 2-Formylbenzimidazoles

Aldehydes of the benzimidazole series have been investigated only in recent years. 2-Formylbenzimidazole [214-217] and its 6-chloro- [217], *N*-methyl-, and *N*-methyl-5-nitro-derivatives [218] are known. The oximes, arylhydrazones, products of condensation with compounds containing a reactive CH_3 group, and certain other derivatives have been obtained [214-219]. A study has been made

of the reaction of 2-formylbenzimidazoles with organomagnesium compounds [220] and their infrared spectra have been examined [221].

2-Formylbenzimidazole is formed in almost quantitative yield on oxidation of bis(2-benzimidazolyl)dihydroxyethylene with sodium periodate [214]:



or on hydrolysis of 2-dichloromethylbenzimidazole (yield 65%). [216] Oxidation of 2-hydroxymethylbenzimidazole [219,222] and 2-methylbenzimidazole with potassium persulphate or selenium dioxide gives less satisfactory results. Complications frequently arise in attempts to obtain *N*-substituted 2-formylbenzimidazoles by the above methods [219].

2-Formylnaphth[1,2-*b*]imidazole forms in 54% yield on oxidation of 2-methylnaphth[1,2-*b*]imidazole with selenium dioxide in acetic anhydride [223].

9. 2-Aminobenzimidazoles

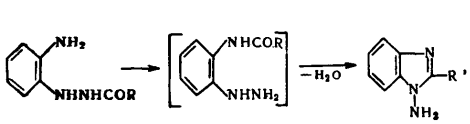
The best methods for the synthesis of 2-aminobenzimidazoles with an unsubstituted NH group is still the reaction of *o*-phenylenediamines with cyanogen bromide [224-227]. Cyanamide has also been suggested for this purpose [228]. 2-Amino-derivatives of 1-alkyl(aryl)benzimidazoles can be obtained by direct amination of *N*-substituted benzimidazoles using sodamide (see below). 2-Amino-1-*p*-nitrophenylbenzimidazole has been synthesised by fusing together guanidinium carbonate and 2-aminophenyl--4′-nitrophenylamine [229]. However, the attempts to use this method for the preparation of 2-aminobenzimidazole and 2-amino-1-phenylbenzimidazole were unsuccessful [202].

2-Guanidinobenzimidazoles form in the reaction between *o*-phenylenediamine and dicyanodiamide or its *N*-alkyl derivatives [230].

10. 1-Aminobenzimidazoles

Ried and Urlass [231] were the first to attempt the preparation of 1-aminobenzimidazoles, by the reduction of *N*-nitrosobenzimidazoles with zinc in acetic acid. However, this resulted only in the removal of the nitroso--group. Lithium aluminium hydride is also unsuitable in this case [232].

1-Aminobenzimidazoles can be obtained by heating acyl derivatives of *o*-aminophenylhydrazines with an aqueous solution of *m*-nitrobenzenesulphonic acid [233], which catalyses this reaction, or with a carboxylic acid [232]:

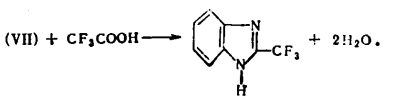


where R = H, CH_3, C_6H_5. When the Phillips procedure (4 *N* HCl) is used, this reaction yields benzo-1,2,4-triazine.

The amino-group in 1-aminobenzimidazoles is readily acylated and reacts with *p*-nitrobenzaldehyde with formation of an azomethine.

11. Fluorobenzimidazoles and Perfluoroalkylbenzimidazoles

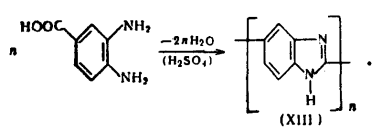
Trifluoroacetic acid and its homologues readily yield 2-perfluoroalkylbenzimidazoles on boiling with *o*-phenylenediamines [234-237]:



Benzimidazoles with a trifluoromethyl substituent in the benzene ring are usually obtained by an indirect procedure [236-241]. 2-Fluorobenzimidazole has not so far been obtained. The fluorine atom in the benzene ring of the benzimidazole molecule can be introduced by the Schiemann reaction [242] or indirectly, starting with fluorophenylenediamines [205,235-240].

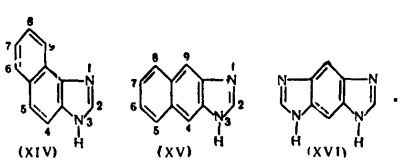
12. Polybenzimidazoles

The first polybenzimidazoles were obtained by Brinker and Robinson [243]. However, attempts, albeit unsuccessful, to obtain polybenzimidazoles of the type of compound (XIII) were made as early as 1953. [244] The synthesis of polybenzimidazole (XIII) in high yield was achieved in 1961 by Marvel and coworkers, who heated 3,4-diaminobenzoic acid in boiling concentrated sulphuric acid [245,246]. Methods for the synthesis of other polybenzimidazoles have also been developed in Marvel's laboratory [247]. All these compounds possess high thermal stability. The mechanism of the reactions resulting in the formation of polybenzimidazoles has been recently investigated by Korshak and coworkers [248]:



C. NAPHTHIMIDAZOLES

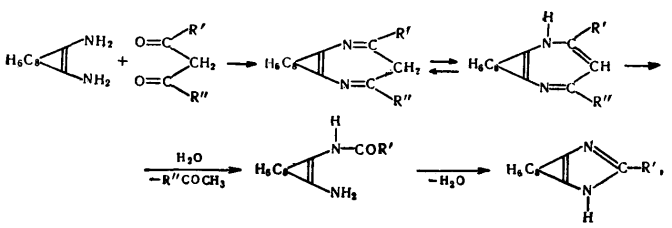
The yield of naphth[1,2-*b*]imidazole (XIV) in the condensation of formic acid with 1,2-naphthylenediamine is low [90]. However, when the sulphate of 1,2-naphthylenediamine is used, the yields of compound (XIV) reach 85% and more [90,249].



Relatively little work has been done on the chemistry of naphth[2,3-*b*]imidazole (XV) because the corresponding diamines are less readily available. The stage involving the cyclisation of the diamines with formic acid into compound (XV) and its 5,6,7,8-tetrahydro-derivative does not present any difficulties [250].

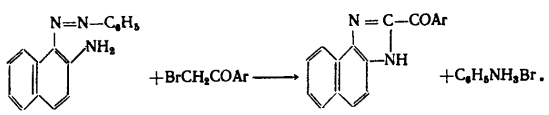
1,2- and 2,3-naphthylenediamines react with 1,3-diketones (acetylacetone, benzoylacetone, dibenzoylmethane) in acetic acid with formation of seven-membered products whose hydrochlorides are almost quantitatively converted

into the corresponding naphthimidazoles after heating with water for a short time [251,252]:



where R′ = CH_3, C_6H_5.

The reactions of acetoacetic and benzoylacetic acids with naphthylenediamines give satisfactory yields of 2-acetonyl(benzoyl)naphthimidazoles. Arylnaphthimidazolyl ketones can be obtained from phenylazo-β-naphthylamine and ω-bromo-ketones [253]:



Like *o*-phenylenediamine, *o*-naphthylenediamines readily react with phosgene, urea, and their sulphur analogues and also with cyanogen bromide, yielding 2-hydroxy(mercapto, amino)naphthimidazoles [226,254,255].

For the synthesis and properties of 1,2,4,5-diimidazobenzene (XVI), see Refs. 256 and 257.

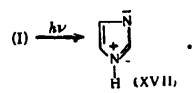
III. PHYSICAL PROPERTIES AND STRUCTURE

A. PHYSICAL PROPERTIES

Both experiment [258-264] and calculation [265-267] show that the dipole moment of imidazole and its derivatives (without polar substituents) is of the order of 3.8–4.0 D. The anomalously high dipole moments of imidazole (6.2 D) and 4-methylimidazole (6.3 D) found by Hückel and Jahneutz [268] are probably due to the fact that the measurements were made in too concentrated solutions where it was impossible to avoid the effect of association.

Substituents of low polarity have little effect on the dipole moments of imidazole derivatives [263]. The nitro-group increases the dipole moment by 2–2.5 D. [263] The replacement of the hydrogen in the NH group by an alkyl has almost no effect on the dipole moment [261,262]. However, *N*-arylation lowers appreciably the dipole moment, due to π-conjugation of the imidazole and aryl rings [264].

Imidazole almost does not absorb in the near ultraviolet, which indicates its high aromatic stability. The absorption in the region 207–208 mμm is due, according to Italian workers [167], to the conversion of symmetric species with a covalent structure into asymmetric and polar species [for example, (XVII)].



(XVII)

The introduction of alkyl groups into any position in the imidazole ring causes a small bathochromic shift of this absorption band [167,269-274] while in *N*- and *C*-arylimidazoles new very intense bands appear in the region 250–300 mμm, characterising the conjugation of the two aromatic rings (Table 1). Bands of this type are also present in the spectra of 2-arylbenzimidazoles [133,167,273-276].

The absorption spectrum of benzimidazole is much more complex. The short-wavelength absorption band (244–248 mμm) is attributed to electron transitions localised in the imidazole ring while the long-wavelength absorption is regarded as a displaced *B*-band of benzene (λ_{max} = 255 mμm). [167,270,277] In the spectrum of benzimidazole, as in those of other benzazoles, there is no absorption band corresponding to the interaction between the condensed benzene and heterocyclic rings. The reason for this phenomenon is still obscure.

The ultraviolet spectra of benzimidazoles have proved useful in the solution of problems associated with the elucidation of the structure of vitamin B_{12}. [278,279] The ultraviolet spectra of 2-imidazolones [212], benzimidazolones [213], 2-aminobenzimidazoles [202,280], and many other derivatives [208,281-284] have also been investigated.

The absorption spectra of naphthimidazoles are still more complex and have not been investigated in detail. There is a marked bathochromic shift in the series imidazole–benzimidazole–angular naphthimidazole–linear naphthimidazole.

The infrared spectra of imidazole [285,286] and its derivatives [283,284,287,288] are characterised by a series of intense absorption bands in the regions 760–880 cm^{-1} (imidazole ring), 1500–1620 cm^{-1} (aromatic C–C and C–N bonds), and 2200–3600 cm^{-1} (NH bond involved in association). The greatest interest attaches to the intense absorption in the region 2200–3600 cm^{-1}, which is attributed to the formation of intermolecular hydrogen bonds of the type $\gtrless N\ldots H-N$ [283,284,288-291] or the formation of the immonium structure $\gtrless N^+-H$. [285] A similar absorption is observed in the infrared spectra of benzimidazole and its 2-substituted derivatives [292], 4,5-diphenylimidazole [293], solutions of the *N*-anilides of imidazolecarboxylic acids [294,295], imidazolones [212], and imidazolethiones [212,296]. When the hydrogen atom of the NH group is replaced by a metal [285], deuterium [286], an acyl group [297], or an aryl group [293] the above absorption disappears, as would be expected.

TABLE 1. Ultraviolet absorption spectra of certain imidazoles.

Compound	λ_{max} and (log ε)	Refs.
Imidazole	207—208 (3.70)	167,269
1-Methylimidazole	212 (3.63)	167
1-Phenylimidazole	225*; 243; 266*; (3.79; 3.84: 3.27)	270
2-Phenylimidazole	271 (4.20)	167
4(5)-Phenylimidazole	257 (4.2)	269
4,5-Diphenylimidazole	225*; 252; 280 (4.23; 4.00; 4.10)	212
Benzimidazole	244; 248; 266*; 272; 279 (3.74; 3.73; 3.69; 3.71; 3.73)	167
Naphth[1,2-*b*]imidazole	222; 240; 273; 279; 313; 319; 326 (4.54; 4.57; 3.63; 3.65; 3.46; 3.38; 3.54)	255
Naphth[2,3-*b*]imidazole	235; 317; 327; 342 (4.79; 3.83; 3.88 3.74)	255

* Inflection.

The Raman [260,285,286,298] and fluorescence [212,299] spectra of imidazole and benzimidazole derivatives have also been investigated.

The nuclear magnetic resonance spectrum of imidazole contains two lines associated with the proton in position 2 and the two protons in positions 4 and 5. [300-305] The proton of the NH group gives rise to a distinct signal only in concentrated benzene and acetone solutions of imidazole and 4(5)-methylimidazole [304].

Imidazoles are amphoteric compounds and therefore the knowledge of the basicity and acidity (for derivatives with an unsubstituted NH group) constitutes some of the most reliable evidence in the elucidation of various structural problems [283,284,290,306-314]. In the series imidazole (pK_a = 7.03)–benzimidazole (pK_a = 5.53)–angular and linear naphthimidazoles (pK_a = 5.28 and 5.24 respectively) there is a decrease in the basicity of the pyridine-type nitrogen hetero-atom. On the other hand, the acidity of the NH group increases in this series (pK_a = = 14.5, 13.2, 12.54, and 12.52 respectively) [255].

The thermodynamic properties of imidazole have been investigated only recently [315]. The enthalpy of formation of imidazole (in the crystalline state) is 14.6 ± 0.8 kcal × × mole^{-1}, its heat of sublimation is 16.0 ± 1 kcal mole^{-1}, and the heat of formation of gaseous imidazole is 30.6 ± ± 1.8 kcal mole^{-1}. These data made it possible to calculate the resonance energy of imidazole as 14.2 kcal × × mole^{-1}. [315,316]

Crystallographic [317], X-ray diffraction [318,319], and semiconductor [320] properties of imidazoles, and their ionophoresis [321] and paper chromatography [322] have been investigated; determinations have been made of the association energy [260,289], the dielectric relaxation time [323], and the ionisation potential [324]; calculations have been made of the dissociation constant in an aqueous medium [289] and of the formal charge on the C and N atoms, using Wheland's equation [308].

B. QUANTUM-MECHANICAL CALCULATIONS ON THE IMIDAZOLE MOLECULE

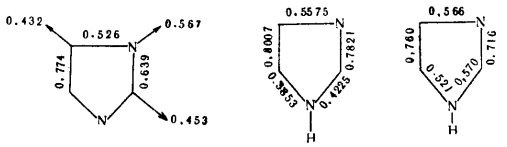
The values given for the π-electron density at various positions in the imidazole molecule (Table 2) are extremely contradictory, which reflects the gradual development of the computational technique by the MO LCAO method. Brown's early calculations [325,326], within the framework of the molecular orbital method, failed to take into account the difference between the two nitrogen atoms in imidazoles and show that in the neutral molecule the electron density in positions 4 and 5 is higher than in position 2, while in the imidazole anion the opposite situation obtains. Brown's latest data, based on the self-consistent field (VESCF) method, which do take into account the difference between the N_1 and N_3 atoms, show qualitatively the same picture [267]. It should be noted that the localisation energies in the imidazole molecule predict a different course of C-electrophilic substitution reactions, which is sometimes found to occur (see below).

TABLE 2. π-Electron density in imidazole.

Neutral molecule					Anion			Cation			Refs.
N_1	C_2	N_3	C_4	C_5	$N_{1(3)}$	C_2	$C_{4(5)}$	$N_{1(3)}$	C_2	$C_{4(5)}$	
1.502	0.884	1.502	1.056	1.056	0.903	1.429	1.323	—	—	—	325
1.479	0.907	1.479	1.067	1.067	0.835	1.458	1.436	—	—	—	326
1.650	1.100	1.401	1.037	1.112	1.197	1.207	1.200	1.512	0.997	0.990	267
0.2308	0.0216	−0.1709	0.037	−0.0853	—	—	—	—	—	—	266
1.347	0.981	1.286	1.104	1.072	—	—	—	—	—	—	327

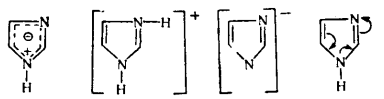
The molecular orbital method has also been used to calculate the reactivity of the benzimidazole molecule [327,328].

Bond orders and free valences in imidazole [266,326,327]:



C. STRUCTURE AND ASSOCIATION

The case of tautomeric transformations, bond equivalence, aromaticity, and the high dipole moment of imidazole are inconsistent with the classical structure (I). For this reason the structural formulae (XVIII)–(XX) have also been proposed for imidazole:



(XVIII) (XIX) (XX)

On the basis of their measurements of the dipole moments (4.8–6.2 D), Hückel and coworkers [268,329] attributed to the imidazole ring the structure of a dipolar ion (XVIII) in which the positive charge is centred on the immonium nitrogen and the negative charge in the centre of the five--membred ring. The calculated dipole moment for this structure (5.5 D) agrees satisfactorily with Hückel's data but is inconsistent with numerous subsequent determinations [258,260-267].

On the basis of data obtained from the potentiometric titration of benzimidazole derivatives, Efros and Porai-Koshits [313] suggested the possibility of the formation of ionic saltlike compounds (XIX) in aqueous solutions. Otting [285] arrived at a similar treatment of the imidazole structure in solid and non-polar media. However, Zimmerman obtained evidence from X-ray diffraction analysis [318], ultraviolet and infrared spectra [271,289,291], acid–base equilibria [289], measurements of the energy of association and mesomerism [289,316], and dipole moments [260] that the saltlike structure (XIX) cannot form.

Analysis of the dipole moments [261-263] shows that the imidazole ring is polarised in the direction of the C–N bond but this polarisation falls far short of that required for the formation of the dipolar structure let alone the ionic structure. The properties of the imidazole ring are most satisfactorily represented by the mesomeric structure (XX). [261,262]

The problem of the causes of the association of compounds containing the imidazole ring with an unsubstituted NH group, is immediately related to the considerations set out above. The investigators who have adopted structures (I), (XVIII), and (XX) for the imidazole ring explain association by the formation of intermolecular hydrogen bonds [259,263,288,290-293,304,305,318,320,325,330]. Nevertheless, Otting [285] attributes the association of imidazole to the formation of an ionic bond in the saltlike structures (XIX).

In Otting's opinion this view is confirmed by the unusual displacement of the NH band to the region 2500–3200 cm^{-1} in the infrared spectrum of imidazole. However, infrared spectroscopic data cannot be regarded as a convincing demonstration that the association of imidazole is of an ionic type, because similar bands (2500–3200 cm^{-1}) are also present in the infrared spectra of compounds which form hydrogen bonds of the type E... HE. [288,331] Furthermore, dilute benzene and acetone solutions of imidazole and 4(5)-methylimidazole do not give rise to a band in the region of 2500–3200 cm^{-1} despite the fact that in such solutions the compounds are present as dimers [292]. At high imidazole concentrations in non-aqueous media the coefficient of association reaches 5–20, [8,290,332] and not 2 as would be expected from Otting's postulate [285],

Finally, other evidence in favour of intermolecular hydrogen bonds as the principal cause of the association of imidazole is the association energy (5 kcal $mole^{-1}$), [289] the distance between the nitrogen atoms in neighbouring molecules (3 Å), [318] and the dependence of the dielectric constant on the concentration of the solutions [262] (the coefficient α varies in the same sense as the concentration [333]).

D. TAUTOMERISM

The isomers of imidazoles with an unsubstituted NH group (the difference between which consists in substituents being present in positions 4 or 5 [8,57,334,335]) cannot be isolated, although they enter into chemical reactions predominantly in one of the tautomeric forms [336–339]. This is due to continuous migration of the proton of the NH group between the two nitrogen atoms of the imidazole ring and also the equivalence of the cations and anions of both isomers. However, there does exist one claim that the above isomers have been separated in the case of sparingly soluble imidazole derivatives [335].

IV. CHEMICAL PROPERTIES

In this section there is no subsection headed "Radical substitution", since homolytic reactions in the imidazole series have been virtually uninvestigated (it is possible that free radicals participate in the formation of 2-mercaptoimidazoles when imidazoles are heated with sulphur [340]). Nor is the extensive class of imidazole metal complexes discussed, a separate review being desirable for these compounds.

In conformity with the guiding principle of this review, in examining the chemistry of arylimidazoles the authors have dealt only with the chemical properties of the imidazole part of the molecule.

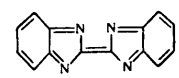
A. AROMATICITY OF THE IMIDAZOLE RING: REDUCTION, OXIDATION, DIENE SYNTHESIS

The imidazole ring is distinguished by high stability with respect to reduction. In the catalytic reduction [22,24,341] of a wide variety of arylimidazoles and furylimidazoles only the aryl or furyl rings reduced and not the imidazole rings, as was believed earlier [342]. The reduction of benzimidazole and its *N*-alkyl derivatives over platinum oxide leads to 4,5,6,7-tetrahydrobenzimidazoles [343]. Naphth[1,2-*b*]imidazole is hydrogenated on the same catalyst to 6,7,8,9-tetrahydronaphth[1,2-*b*]imidazole, while phenanthr[9,10-*b*]imidazole is reduced to an octahydro-derivative [343].

However, 2-methyl-4,5-diphenylimidazole may be reduced over a palladium catalyst to 2-methyl-4,5-diphenylimidazolidine [18]. In the reduction of benzimidazole with lithium aluminium hydride, Bohlmann obtained a substance to which he attributed on inadequate grounds the structure of 2,3-dihydrobenzimidazole [344]. Bayer showed that imidazole and benzimidazole are hydrogenated in acetic acid over platinum oxide *NN'*-diacetylimidazolidine and *NN'*-diacetylbenzimidazoline [345]. The corresponding derivatives of 2,3-dihydroimidazole are formed on addition of the dimethyl ester of acetylenedicarboxylic acid to 1,2-dialkylimidazoles in a reaction of the Diels–Alder type [346,347] (*cf.* Refs. 348 and 349).

The imidazole ring is more stable than benzene and naphthalene rings in oxidation reactions, as shown by the oxidation of benzimidazole with potassium permanganate, potassium dichromate [31–34], or hydrogen peroxide [350] to imidazole-4,5-dicarboxylic acid. In the oxidation of naphth[1,2-*b*]imidazole the product is 4-(*o*-carboxyphenyl)-5-carboxyimidazole and not imidazole-4,5-dicarboxylic acid [10]; napth[2,3-*b*]imidazole is oxidised to imidazo-4,9-naphthoquinone [249].

The oxidation of benzimidazole with lead peroxide [351] is quite unusual, leading to the formation of $\Delta^{2,2'}$-diisobenzimidazolidene (XXI). The same substance was also obtained in the oxidation of 2,2'-dibenzimidazolyl with PbO_2: [351]



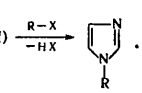
(XXI)

Selenium dioxide in dioxan oxidises 2-methylbenzimidazole to *o*-hydroxyacetanilide [352].

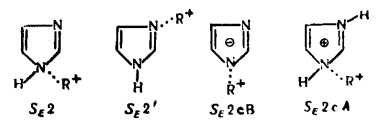
B. ELECTROPHILIC SUBSTITUTION

1. *N*-Substitution

In this section we shall consider the methods of direct introduction of substituents into position 1 of the imidazole ring (indirect methods have been examined above). Disregarding the mechanism of the process, the reaction may be represented in a general form as a simple substitution of the hydrogen atom of the NH group by a radical R:

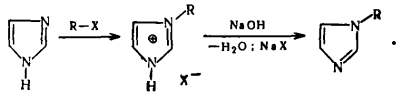


a. Alkylation of imidazoles. Reaction mechanisms. *N*-Substitution in the imidazole ring is by no means as simple as is suggested in a number of reviews [8–10]. It must be borne in mind that, depending on the conditions, imidazole can enter into alkylation reactions in several forms (sometimes several forms at the same time) — as a base (S_E2 and S_E2' mechamisms), anion (S_E2 cB mechanism), or as the conjugate acid (S_E2 cA mechanism):

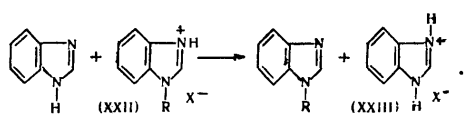


S_E2 S_E2' S_E2cB S_E2cA

The classical method for the preparation of *N*-alkylimidazoles consists in the reaction between the heterocyclic compound and an alkyl iodide (bromide, or, less frequently, chloride) in a sealed tube at 100–150° (Wallach, Wyss, Fischer, Pyman)[8–10]. Under these conditions the reaction involves preferentially the pyridine-type nitrogen atom (S_E2' mechanism)[337,353]:



If the process stopped at the stage in which the hydrochloride of the *N*-substituted derivative is formed, this method could yield the theoretical amount of 1-alkylimidazole (after treating the salt with alkali). However, in fact the yield of the *N*-substituted derivative when imidazole is alkylated in a neutral medium reaches 50% at most. Using benzimidazole as an example, it has been shown that the initial base which fails to enter into the main reaction then reacts with the hydrochloride of benzimidazole[353] and the resulting 1-alkylbenzimidazole is further alkylated with the alkyl halide to a 1,3-dialkylbenzimidazolium salt. Thus these side-reactions lead to an irreversible conversion [the conjugate acids (XXII) and (XXIII) cannot undergo further alkylation[337,353]] of about 50% of the starting compound into benzimidazolium (XXIII) and 1,3-dialkylbenzimidazolium salts. The use of two moles of imidazole (to bind the HX) per mole of the alkylating agent cannot be regarded as a successful solution of this problem:

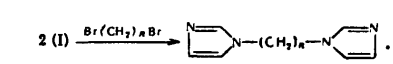


The most satisfactory results are obtained when imidazoles are alkylated in the presence of alkaline agents. Apart from alkali metal hydroxides, sodium alkoxides[354,357], sodium acetate[358], sodium carbonate[359], sodamide[360–363], sodium hydride[348], etc. have been used. The reaction is carried out in alcohol, less often in hydrocarbons[354,362], water[359], dioxan[360,363,364], acetone[366], and liquid ammonia[361,365].

The enhanced nucleophilic character of the nitrogen atoms in the imidazole anion makes it possible to achieve the alkylation at a lower temperature and thereby avoid the formation of a large amount of quaternary salts. In the case of benzimidazole it is permissible to vary the initial amounts of alkyl halide and alkali in order to improve the yield[366]. The maximum yield of 1-alkylbenzimidazole (76–83% for primary and 50–60% for secondary alkyl and aralkyl bromides) can be achieved by using two moles of alkyl bromide and 1.5 moles of alkali per mole of benzimidazole.

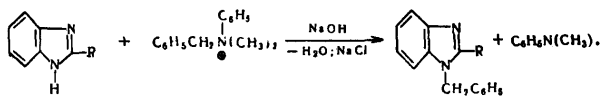
The ease of formation of quaternary salts constitutes a serious obstacle in the alkylation of imidazole itself, since the latter is much more basic than benzimidazole. Here it is almost impossible to use an appreciable excess of the alkylating agent and temperatures higher than 20–40°.[355,361,367] Best results are obtained when imidazole is alkylated in liquid ammonia in the presence of sodamide[361].

Bis(1-imidazolyl)alkanes are formed in the reaction of benzimidazole[368] and imidazole[369] with dibromoalkanes:



In the presence of alkaline agents the imidazole ring is readily alkylated with ethylene chlorohydrin[370,371], chloroacetic acid or its ethyl ester[132,372,373], and dialkylaminoalkyl chlorides[363,374–376].

It is extremely convenient to introduce primary aralkyl radicals (benzyl, α-naphthylmethyl, etc.) into the NH group of benzimidazole by allowing the latter to react with dimethylphenylaralkylammonium chlorides[219,353,377,378]. The reaction proceeds rapidly and almost with a quantitative yield in an aqueous solution of sodium hydroxide:



In the imidazole series this reaction has not been investigated.

The use of the silver salts of imidazoles or *N*-chloromercuri-imidazoles is the only method available for the introduction into position 1 of the imidazole ring of substituents such as triphenylmethyl[379,380] or glycosyl[381–389]. The alkylation of 2-arylbenzimidazoles in an alkaline medium proceeds with considerable difficulty because of steric hindrance[133,353]. In this case it is also desirable to use the corresponding silver salts.

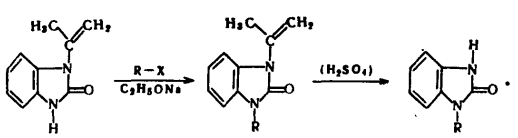
As a result of the formation of two isomers, the alkylation of asymmetric imidazole and benzimidazole derivatives proceeds in a very complex manner. This problem has been recently thoroughly reexamined on the basis of information derived from kinetics and spectroscopy[337,338]. The data obtained are however inconsistent not only with the old results but also with the results of many new studies[358,390–392] and therefore final conclusions would probably be premature. Also contradictory are the results obtained on the alkylation of the asymmetric napth[1,2-*b*]-imidazole[8,10,90,393]. There is a review of work done on the alkylation of asymmetric imidazoles[353].

Benzimidazoles[394,395], benzimidazolones[396], and benzimidazolethiones[397] react with formaldehyde and secondary amines (Mannich reaction), forming *N*-aminomethyl derivatives.

The reaction of benzimidazole derivatives with ethylene oxide, yielding *N*-β-hydroxyethylbenzimidazoles, has been investigated in detail[398–400].

Imidazole, benzimidazole, and their substituted derivatives are alkylated at the NH group by a wide variety of unsaturated compounds: acetylene[401,402], acrylonitrile[313,392,403] and other derivatives of acrylic acid[404,405], and vinyl acetate[406]. The methylation of imidazole with diazomethane proceeds smoothly[393,407,408].

The reaction of *o*-phenylenediamine with acetoacetic ester in a neutral medium gives 1-isopropenylbenzimidazol-2-one, from which *N*-monoalkyl derivatives of benzimidazolone can be obtained[356,357]:

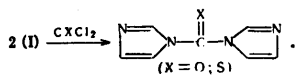


2-Mercapto-derivatives of imidazole [36,409-413] and benzimidazole [204,414,415] are alkylated with alkyl halides [36,409,410,204,414,415], α-halogeno-ketones [411,412], α-halogeno--aldehydes [412], and α-halogeno-acids [35,413]: the reaction involves initially the SH group, this being followed by *N*-alkylation.

In alkaline [225] and neutral [416,417] media 2-aminobenzimidazoles are alkylated at the ring nitrogen.

b. *N*-Arylation of imidazoles. Until recently the only example of direct *N*-arylation of the imidazole ring was the ready synthesis of *N*-dinitrophenyl- and picryl--imidazole derivatives, starting with 2,4-dinitrohalogenobenzenes and picryl chloride [293,418-420]. Not long ago a method was developed for the direct arylation of imidazole and benzimidazole with aryl halides, without substituents activating the halogen atom in the arylating agent [421,422]. The reaction is carried out in nitrobenzene in the presence of potassium carbonate and cuprous bromide (catalyst). The yield of *N*-aryl derivatives reaches 73%. The replacement of nitrobenzene by other solvents (tetralin, diethylaniline, excess of aryl bromide) gives worse results.

c. Acylation of imidazoles. Studies made in the 1950's established that *N*-acylimidazoles and their reactions are of fundamental importance in enzymic transacylation [6,7]. Staab synthesised unusually reactive acylimidazoles which served as models for the most important biochemical reactions (see Staab's review [423]):



Imidazolides of this type have found application in the synthesis of aldehydes, amidines, esters, acid anhydrides, and in peptide synthesis [424,427], the last application being particularly important.

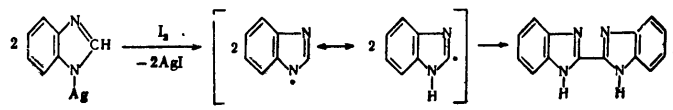
N-Formylimidazoles [428] and *N*-benzyloxycarbonylimidazoles [429] can be used as formylating and benzyloxycarbonylating agents.

The reaction of imidazole with potassium thiocyanate in a neutral medium yields *N*-carbamoylimidazole [430], while aryl cyanates react with imidazoles in a more complex manner, involving not only the N but also the C_2 atom [431].

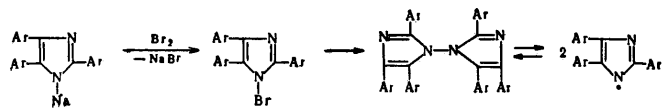
The chlorides of aromatic sulphonic acids readily acylate imidazole and benzimidazole at the NH group in the presence of weakly basic agents (potassium carbonate, sodium acetate) [432-434].

2-Mercapto- and 2-hydroxy-derivatives of imidazole and benzimidazole are acylated with acid anhydrides and chlorides at the N atoms [435-437]. 2-Aminobenzimidazoles are acylated at the exocyclic amino-group [416]. In the reaction of acetic anhydride with the *N*-oxide of benzimidazole the product is 1,3-diacetylbenzimidazolone [437] and not 1-acetyl-2-acetoxybenzimidazole [438].

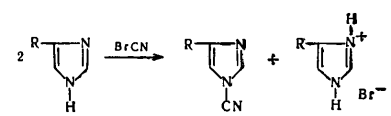
d. Halogenation and cyanation. It has been established that the product obtained [8,9] by the action of iodine on an alkaline solution of benzimidazole is *N*-iodobenzimidazole and not the 2-iodo-derivative [439,440]. It might have been supposed that on reaction with iodine the silver salt of benzimidazole would also yield *N*-iodobenzimidazole and then the hitherto unknown *NN'*-dibenzimidazolyl. Actually the reaction is more complicated, apparently involving the 2-benzimidazolyl radical, and leading to the formation of 2,2'-dibenzimidazolyl [351]:



Imidazole reacts with halogens, yielding *C*-substituted derivatives, but it has been demonstrated convincingly [441] that here too the intermediates are *N*-halogenoimidazoles (*trans*-halogenation). For example, the reaction between the sodium salts of 2,4,5-triarylimidazoles and bromine in absolute ether gives *NN'*-diimidazolyls, since the intermediate *N*-bromoimidazoles formed in this reaction cannot undergo a rearrangement to the *C*-bromo-derivatives [441]. The N–N bond in diimidazolyls readily undergoes homolytic splitting with formation of two *N*-imidazolyl radicals [441,442]:

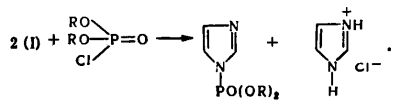


Cyanogen bromide is known [8] to react with *N*-substituted imidazoles with formation of 2-bromoimidazoles. Imidazoles with a free NH group undergo *N*-cyanation [443]:

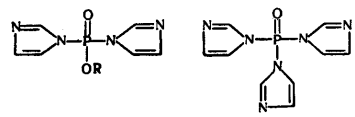


where R = H, CH_3. Cyanogen bromide introduces the CN group into 2-mercaptoimidazole at the SH group [444].

e. Phosphorylation. *N*-phosphorylimidazoles play an important role in enzymic transphosphorylation [6]. They form in the reaction of two moles of imidazole or benzimidazole with one mole of a dialkyl(diaryl)phosphoric acid chloride [445,446].



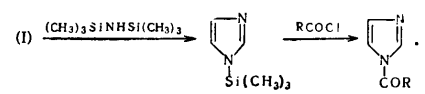
Di- and tri-imidazolides of phosphoric acid can be obtained similarly from phosphoric acid dichloride or from phosphorus oxychloride [447,448]:



The reaction between *NN'*-carbonyldiimidazole and phosphoric acid esters also yields *N*-phosphoroimidazoles [449]. *N*-phosphoroimidazole is extremely unstable and rapidly undergoes autocatalytic hydrolysis. Its derivatives, in which the phosphoryl residue is combined with an organic radical, are more stable. These compounds readily phosphorylate amines, alcohols, and the carboxy--group at room temperature [450].

f. Silylation. Imidazole, benzimidazole, and other heterocyclic compounds with a nitrogen atom of the pyrrole

type react with hexamethyldisilazane with formation of *N*-trimethylsilyl derivatives[451], which exhibit remarkably high reactivity. They are acylated with the chlorides of organic and mineral acids with almost quantitative yields even at 0°:



g. Nitrosation. When an acetic acid solution of benzimidazole and its 2-substituted derivatives is treated with aqueous sodium nitrite, *N*-nitrosobenzimidazoles, giving a positive response to the Lieberman test, are formed[173,231].

2. *C*-Substitution

Electrophilic substitution (azo-coupling, nitration, halogenation, etc.) of the carbon atoms in the imidazole ring is characteristic only of imidazole itself and those condensed systems in which the imidazole ring is linked to a non-aromatic ring: tetrahydrobenzimidazole, phenanthr[9,10-*b*]imidazole, etc.[90] For compounds such as benzimidazole or naphthimidazoles, nucleophilic substitution reactions at the 2-carbon atom of the imidazole ring (see below) are typical, as a result of the electrophilic effect of the aromatic ring condensed with the imidazole ring.

One of the classical problems of imidazole chemistry is associated with electrophilic substitution. Only in recent years has it become more or less clear why in some cases (nitration, sulphonation, etc.) electrophilic substitution takes place at positions 4 and 5 of the imidazole ring while in others (coupling with diazonium salts) position 2 is involved. As late as 1950 Schofield suggested that the imidazolium cation is involved in nitration and sulphonation while the neutral molecule is involved in the coupling reaction[452] (the latter hypothesis subsequently proved to be erroneous). Kinetic studies of iodination[453] and diazo-coupling[454] of imidazole and molecular-orbital calculations[325,326] made a decisive contribution towards the solution of this problem. It was found that the mechanisms of the halogenation and coupling reactions involve the formation of the conjugate base of imidazole (iodination proceeds via the imidazole anion B^- even at pH 7). This is confirmed by the fact that 1-methylimidazole does not undergo the coupling reaction. Furthermore, deuteration of imidazole in a neutral medium with D_2O leads to 4(5)-substitution, while in NaOD solution the C_2 atom is deuterated preferentially[300].

The data on the halogenation of imidazole are contradictory. Earlier it was found that bromination proceeds preferentially in position 4(5), while iodination leads to a 2-substituted derivative. However Ridd[454] reported that, even in the presence of a 20-fold excess of imidazole, the main iodination product is the di-iodo-derivative (see also Refs. 455 and 456). Study of the iodination of deuteroimidazoles (the kinetic isotope effect method) showed that the iodination proceeds, like bromination, in position 4(5).[457] This finding lent support to Brunings'[458] hypothesis of primary *N*-iodination of imidazole with subsequent rearrangement of the *N*-iodoimidazole to the *C*-iodo-derivative. The kinetic equation for the iodination of imidazole includes, in addition to the term corresponding to the reaction of the imidazole anion with the I^+ or H_2OI^+ cations, a second term which depends on the concentration of imidazole and indicates that the reaction may be catalysed by imidazole itself:

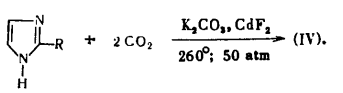
$$V = k[B^-][H_2OI^+] + k'[B^-][BHI^+].$$

This finding can be understood as a special case of a *trans*-reaction with participation of the imidazole ring. Recently yet another report of the conversion of *N*-bromoimidazoles into *C*-bromo-derivatives has appeared[441]. We may also recall that in an alkaline medium benzimidazole is iodinated at the N atom[439,440].

How then can we explain why two reactions, iodination and coupling, apparently equivalent as regards mechanism and involving the same intermediate (imidazole anion), result in attack at different positions? As stated above, molecular-orbital calculations on the conjugate base of imidazole lead to two different conclusions: the charge densities suggest that electrophilic substitution should occur in position 2, while according to the values of the localisation energies, electrophilic agents should attack the imidazole rings in positions 4 and 5. It is believed that in the above two reactions iodination follows the values of localisation energies, i.e. depends on the transition state of the reaction, in which the removal of the proton determines the rate of the process as a whole. The overall kinetics of imidazole iodination are very complex and the reason for the instantaneous iodination of the monoiodo-compound to give the di-iodo-derivative still remains obscure. Certain phenylimidazoles substituted in position 2 can couple with diazonium salts also in position 4(5).[464]

In the presence of sodium ethoxide, pentyl nitrite nitrosates phenylimidazoles with an unsubstituted NH group in position 4(5). If positions 4 and 5 are occupied, nitrosation in position 2 does not occur. The properties of the resulting 4(5)-nitrosoimidazoles have been investigated in detail[459-465].

The synthesis of imidazole-4,5-dicarboxylic acids by the reaction of carbon dioxide with imidazole and its 2-alkyl derivatives constitutes a new electrophilic substitution reaction in the imidazole series[466]:



Sulphur tetrafluoride converts both carboxy-groups of the acid into trifluoromethyl groups[467].

It has been known for a long time that formaldehyde or paraformaldehyde hydroxymethylate *N*-substituted imidazoles in position 2. Unexpectedly this reaction was achieved also with *N*-vinylbenzimidazole[468]. It would be desirable to verify this unique electrophilic *C*-substitution reaction in the imidazole ring of benzimidazole.

N-substituted imidazoles undergo thermal condensation with aliphatic (except for acetaldehyde) and aromatic aldehydes with formation of imidazol-2-yl carbinols[361], which can also be obtained by the action of the aldehydes on 2-lithioimidazoles[361,469].

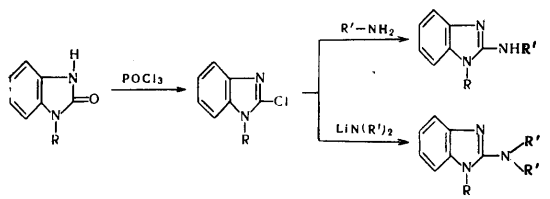
C. NUCLEOPHILIC SUBSTITUTION

In monographs and reviews on the chemistry of imidazole[8-15] little attention has been given to nucleophilic

substitution, because reactions of this type in the imidazole series began to be investigated systematically only in recent years.

1. Substitution of Groups in Position 2 of the Imidazole Ring

The first example of nucleophilic reactions in the imidazole series is the synthesis of 2-chlorobenzimidazole from benzimidazolone and phosphorus oxychloride[470]. Later this reaction was studied in detail[440] and extended to 4,5-diphenylimidazolone[471], benzimidazolone derivatives[201,202,393,471-478], naphthimidazolone[479], and tetrahydronaphthimidazolone[480]. The chlorine atom in position 2 of the imidazole ring can be relatively readily exchanged for amino-, alkylamino-, arylamino-, and hydrazino-groups[255,393,440,472,475,477,480,484]:

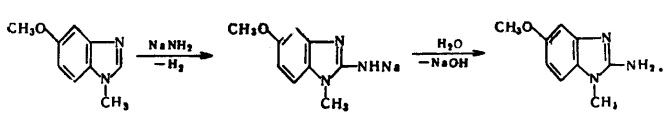


where R′ = alkyl, aryl, NH_2. Chlorine is exchanged even more readily in quaternary benzimidazolium salts[485].

It should be noted that all these reactions have been mainly investigated for condensed systems containing the imidazole ring, but not for imidazole itself. Other groups in position 2 of the imidazole ring also exhibit considerable mobility. Thus the methylthio-group can be exchanged for amino-, benzylamino-[255], and hydrazine-groups[481]. The sulpho-group is readily replaced by chloro-[485], hydroxy-, alkylamino-, and cyano-groups[9]. The ready hydrolysis of sulphones of the benzimidazole series probably belongs to the same class of reactions[486,487].

2. The Action of Sodamide on Imidazole Derivatives (Chichibabin Reaction)

By allowing sodamide to react with 5-methoxy-1-methylbenzimidazole in xylene, Simonov and Uglov obtained the corresponding 2-amino-derivative in good yield[488]:



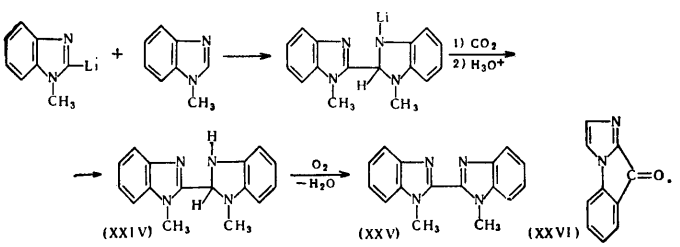
Later this reaction was extended to other *N*-alkyl, aralkyl, and aryl derivatives of benzimidazole[90,202,368,375,377,378,433], naphth[1,2-*b*]imidazole, and tetrahydronaphth[1,2-*b*]imidazole[489]. Heterocyclic compounds with an unsubstituted NH group are not aminated by sodamide, since the anion formed initially, clearly cannot be subject to nucleophilic attack[433,488].

Apart from the formation of the 2-amino-derivative, in the amination of *N*-arylbenzimidazoles the imidazole ring opens as a result of the p,π-conjugation of the *N*-aryl and imidazole rings with consequent loss of aromaticity by the latter[202,264].

Amination of *N*-alkylbenzimidazoles substituted in the benzene ring showed that this reaction is significantly influenced by the nature of the substituent in position 5 of the benzene ring. Whereas 5-alkyl- and 5-alkoxy-1-alkylbenzimidazoles form 2-amino-derivatives, 5-hydroxy-, 5-halogeno-, 5-nitro-, and 5-carboxy-derivatives do not enter into this reaction[490,491]. Attempts to extend the Chichibabin reaction to *N*-alkyl derivatives of 4,5-diphenylimidazole, 4,5,6,7-tetrahydrobenzimidazole, and phenanthr[9,10-*b*]imidazole were unsuccessful[492]. Thus amination of the imidazole ring at the 2-carbon atom occurs only when the former is condensed with an aromatic ring (in 4,5-diphenylimidazole the phenyl rings are not coplanar with the imidazole ring while in phenanthrimidazole the aromaticity of the middle benzene ring of phenanthrene cannot be compared with the aromaticity of the benzene ring in benzimidazole — a well known fact). From this point of view, the derivatives of imidazole itself should not enter into the Chichibabin reaction either.

3. Metalation Reactions

N-alkylimidazoles[361,469] and *N*-alkylbenzimidazoles[365] undergo metalation under the action of butyl-lithium at low temperatures with formation of 2-lithio-derivatives. In the metalation of 1-methylimidazole a small amount of the 5-substituted derivative also forms[469]. The reaction of butyl-lithium with 1-methylbenzimidazole at room temperature yields the corresponding 2,2′-dibenzimidazolyl (XXIV) and its dihydro-derivative (XXV), which can be explained by the following mechanism[365]:

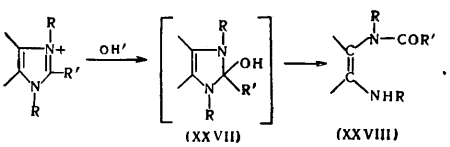


1-Alkylbenzimidazoles are also readily metalated in position 2 by phenyl-lithium[122] and phenylsodium[493].

The reaction of 1-phenylimidazole with an excess of butyl-lithium followed by reaction with carbon dioxide leads to the formation of 4-oxoimidazo[1,2-*a*]indoline (XXVI), which also constitutes evidence that the imidazole ring is metalated at the 2-carbon atom[469]. *N*-arylbenzimidazoles are not metalated by butyl-lithium at low temperature but at room temperature butyl-lithium adds to the C–N bond[122], a reaction which was observed earlier also for *N*-methyl-2-t-butylbenzimidazole[494].

4. Imidazolium Salts and Their Reactions

1,3-Dialkylimidazolium salts are known to be converted under the action of bases into the so-called "pseudo-bases". This reaction is a consequence of the nucleophilic attack by the hydroxide ion on the C_2 atom of the imidazole ring[418,419,495]:



Pseudo-bases have been regarded for a long time as cyclic carbinols (XXVII) and it was not until a study had been made of their infrared spectra and their acylation reaction that their non-cyclic structure (XXVIII) was established [293,418,419,496]. The existence of a ring–chain tautomerism between the cyclic and non-cyclic forms has been suggested [495].

The benz- and naphth-[1,2-*b*]imidazolium salts, containing the 2,4-dinitrophenyl substituent at the N atom are converted irreversibly into derivatives of 2-amino-2′,4′-dinitrodiarylamine even under the action of bases as weak as aniline and pyridine [418,419] (*cf.* Ref. 497). The conversion of 4,5-diphenylimidazolium and 4,5,6,7-tetrahydrobenzimidazolium salts occurs similarly although under somewhat more severe conditions (ammonia, sodium carbonate) [498,499].

ADDED IN PROOF

After this review had been sent for editing, the following papers were published:

On Physical Properties

Spectra: infrared [500,501], nuclear magnetic resonance [502], ultraviolet [503].
Phototropic transformations and chemiluminescence [504–507].

On 1-Substituted Imidazoles

Methylation of 2-perfluoroalkylimidazoles with diazomethane [508].
Preparation of 1-vinylimidazoles [509].
New synthesis of glucopyranosides of benzimidazole [510].
Acylation of benzimidazoles [511].
Acylation of the OH group of serine with *N*-acetyl derivatives of histidine [512].
New stereospecific synthesis of olefins from 1,2-diols and *NN*′-dithiocarbonylimidazole [513].
Imidazolide method for the preparation of diacetyl peroxides and per-acid esters [514].
N-Carbamoylimidazoles [515].
N-hydroxyimidazoles [516] and benzimidazoles [517–520].

On 2-Substituted Imidazoles

Syntheses of 2-nitroimidazole (azomycin) [521], 2-aminoimidazole [522], 2-arylaminoimidazole [523], 2-arylaminobenzimidazole [524], 2-piperidino-2-dimethylaminobenzimidazole [525].
Reaction of 2-aminobenzimidazoles with halogeno-esters [526].
Synthesis and reactions of 1-phenyl-2-hydrazinobenzimidazole [527].
Benzimidazol-2-ones [528] and dihydrobenzimidazoles [529,530].
Benzenesulphonyl- and methanesulphonyl-benzimidazolones [531].
Nucleophilic substitution of chlorine in 2-chlorobenzimidazoles: preparation of 2-hydroxy- and 2-mercapto-benzimidazoles [532,533].
2-Acetyl- and 2-benzoyl-benzimidazoles [534].
Structure and chemical properties of 2-formylbenzimidazoles [535].
Preparation of 2-mercaptobenzimidazole by direct thiolation of benzimidazole [536].
2-Imidazolone and its derivatives [537].
2-Aroyl-4(5)-arylimidazoles [538,539].
Formation of 2-acylbenzimidazole from *N*-acylaminophenylpiperidine and its homologues [540].
2-Cyanomethyl- [541] and 2-(5-thienyl)benzimidazoles [542].
Synthesis of benzimidazoles from *N*-arylamidines (thiabendazole) [543].
2-Arylbenzimidazoles from *o*-phenylenediamines and carboxylic acid hydrazides [544].
2-Substituted benzimidazoles from *o*-phenylenediamine and carboxylic acids [545].
Perfluoroalkyl- [546] and polyfluoro-benzimidazoles [547].
Synthesis of 1,2,4,5-tetra(benzimidazol-2-yl)benzene [548].
[Thermal decomposition of benzylidene-2-azidoanilines [549] (Ed. of Translation)].
2-Styrylbenzimidazoles from *o*-phenylenediamines and cinnamic acid [550].
Bis-(2-benzimidazolyl)alkanes [551].

On 4(5)-Substituted Imidazoles

4(5)-Halogeno- and 4,5-dihalogeno-imidazoles [552–554].
Nitration of 2-methylimidazole [555].
4(5)-Nitroimidazoles [556].
4,5-Diaminoimidazoles [557].
4(5),4′(5′)-Polymethylenediimidazoles [558].
Cyclo-octyl- and cyclononyl-imidazoles [559].

On the Reactivity of the Imidazole Ring [560–562].

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REACTION OF NUCLEIC ACIDS WITH METALS

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1. INTRODUCTION

Nucleic acids play an important part in the processes of the biosynthesis of protein, growth, reproduction, and heredity of living organisms. However, even now very little is known about the actual mechanism of their participation in these processes; this explains the considerable interest of investigators in the various types of reaction of nucleic acids.

In recent years it has been found that nucleic acids react with ions of many metals, the result being a change in several properties of the acids. It is extremely probable that the reaction with metals is of great importance in the biological functions of nucleic acids but there have been very few investigations in this direction and there is still no direct proof that metals play an essential part in the biological functions of the nucleic acids.

The study of the reactions of complex formation between metals and nucleic acids is also of independent interest in connection with the search for so-called electronic stains for electron microscopy of nucleic acids (metal ions in compounds with the nucleic acids can act as electron dyestuffs) and for obtaining especially pure preparations of nucleic acids.

In order to understand the reactions which take place between metals ions and nucleic acids, we will briefly consider the structure and properties of the latter.

2. STRUCTURE AND PROPERTIES OF NUCLEIC ACIDS

The nucleic acids are linear polymers [1] the chains of which are composed of residues of phosphoric acid, pentoses [deoxyriboses in deoxyribonucleic acid (DNA) and riboses in ribonucleic acid (RNA)] and heterocyclic nitrogen bases (purines and pyrimidines).

Sections of the polymeric chains of DNA and RNA are shown in Fig. 1, which represents conventionally four links in each chain. The monomer links differ from one another in the structure of the purine or pyrimidine bases. The natural long molecules of nucleic acids consist of many thousand differently alternating monomeric links. It is evident from Fig. 1 that the DNA chain differs from the RNA chain not only in the composition of the sugars but also in the composition of the pyrimidine bases. The thymine present in DNA is replaced by uracil in RNA.

X-Ray diffraction study of films of nucleic acids showed that the DNA structure is much more ordered than the RNA structure, and that DNA is a two-chain spiral, diameter 20 Å and length of turn 34.6 Å. A turn of the spiral contains ten monomeric links. The lateral groups — purine and pyrimidine bases — are packed in the centre of the spirals.

According to the model of Crick and Watson[2], these bases in the two-chain DNA molecule are located in such a manner that the adenine in one chain is always opposite the thymine in the other, and the guanine is opposite the cytosine. The two chains are connected with one another by hydrogen bonds (see Fig. 2).

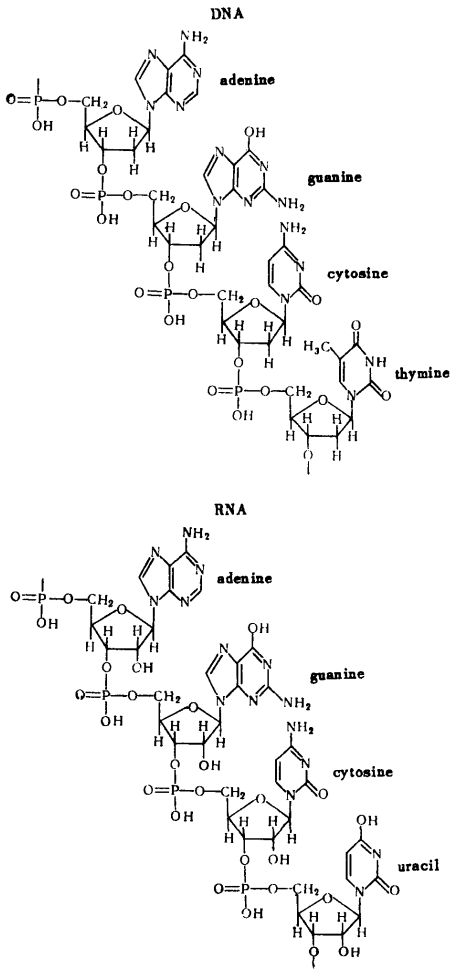


Fig. 1. Sections of the polymeric chains of DNA and RNA.

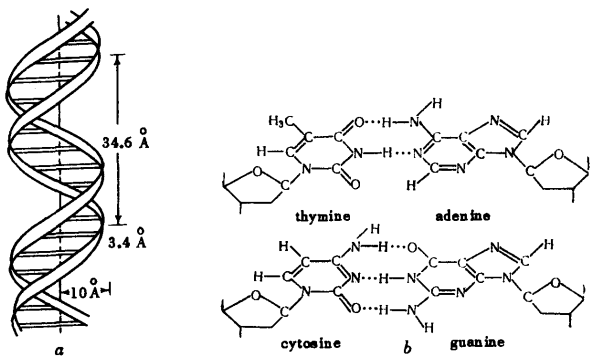


Fig. 2. Macromolecular structure of DNA: *a*) two spirals: phosphato-deoxyribose chains; horizontal lines: pairs of nitrogenous bases connecting the two chains by hydrogen bonds; *b*) hydrogen bonds in pairs of bases.

The RNA molecule consists of one flexible polynucleotide chain, the configuration of which is not stable and fixed, but is determined by the surrounding medium[3-6]. Thanks to the hydrogen bonds, in some places the RNA chain is turned into a double filament, formed by separate turns of the spiral. Between the turns, single-chain sections are situated randomly. This secondary structure of RNA in turn does not remain stable — depending on the conditions of distribution of the spiral portions it can become ordered: more complex compact tangles of tertiary structure are formed. Fig. 3 shows the macromolecular structure of RNA[5].

The hydrogen bonds create a definite structural rigidity in nucleic acids, which is evidently a general characteristic of the macromolecules of biopolymers and determines their biological function[7]. The destruction of the hydrogen bonds of isolated nucleic acids is observed over a narrow range of temperatures, in which "fusion" of the intramolecular regular structure occurs with change of the spirals into disordered tangles[8]. This process is termed denaturing. The change from the native stage into the denatured ("phase transformation") can occur not only on heating,

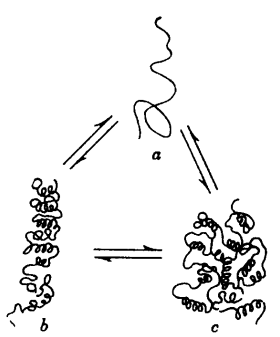


Fig. 3. Macromolecular structure of RNA: *a*) primary structure — loose, random tangle or straightening chain; *b*) secondary structure — compact rod with more or less ordered orientation of the double-spiral portions; *c*) tertiary structure — compact tangle with spiral portions.

but also as the result of other factors. This transformation can be followed by the change in light absorption of solutions of nucleic acids in the ultraviolet region.

In the spectrum of the nucleic acids there is an absorption band in the near ultraviolet region, which is due to light absorption by the chromophoric groups of the heterocyclic bases. The maximum of the band is approximately at 260 mμ. The optical density of native nucleic acids is ~ 40% less than the total optical density of their monomer constituents. This fall (hypochromic effect) is explained by the parallel arrangement of the chromophoric groups of the bases in the native preparations. The optical density rises during denaturing. This hyperchromic effect is explained by the destruction of the parallel arrangement of the chromophoric groups of the bases during the phase transformations from the spiral-shaped ordered forms to the less ordered. The decrease in optical density thus shows the increase in the structural rigidity of nucleic acids due to the increase in spirilisation, but an increase in optical density shows their degradation into disorientated chromophoric groups, in any breakdown of ordering [1,9-12].

Some information about the dimensions, form, and molecular weight of the nucleic acid macromolecules was obtained by sedimentation analysis and measurements of viscosity and diffusion rates [13].

3. EFFECT OF METAL IONS ON THE PROPERTIES OF NUCLEIC ACIDS

The nucleic acids isolated from different biological objects usually contain insignificant amounts of ions of one or more metals [14-28]. Thus Wacker and Vallee [29] reported the presence of chromium, nickel, iron, manganese, zinc, and other metals in preparations of DNA and RNA. The concentration of some metals in nucleic acids of different origins is constant, but the bond between the metals and nucleic acid is so strong that they are removed with difficulty even using such strong chelating reagents as ethylenediaminetetraacetic acid, quinolin-8-ol, dithizone, etc.[29] These facts are evidence that the metals form chemical bonds with the nucleic acid macromolecules.

It was stated above that there are still no direct proofs of the participation of metals in the biological function of the nucleic acids. However, it is suggested that the metal ions bring about a bond between the nucleic acids and proteins [30], play a fundamental part in the structure and function of nucleoproteins [31,32], and affect the synthesis of proteins and the transmission of heredity information [29]. Gol'dshtein and Gerasimova [33] think that Fe^{3+} ions have a special role in the function of DNA: they take part in the formation of bonds between separate chains of DNA and as a result are able to regulate the denaturing of DNA, and are also the cause of the enzymeless transverse cleavage of the DNA molecule. According to the hypothesis of Ivanov [34] the biosynthesis of DNA is linked with the redox changes of iron or copper ions during their chelation with DNA, in which the oxidation of the metal ions brings about a weakening of the bonds between the complementary pairs of DNA bases, and reduction the stabilisation of the double-track conformation of DNA. Ascorbic acid, which participates in the synthesis of DNA in the cell, is a possible electron carrier in the oxidation and reduction of iron in DNA [35]. The correctness of this type of hypothesis is confirmed by the change in the properties of isolated nucleic acids and nucleoproteins under the action of ions of various metals. We will list some of these factors.

The dimensions and form of nucleoproteins suspended in cytoplasm and the degree of their polymerisation depends on the concentration of magnesium ions in the medium [32,36-38]. Alkaline earth metal ions affect the structure and properties of chromosomes [39-44]. In the presence of metal ions RNA is stable in relation to the action of ribonuclease [45,46], the macromolecular configuration of RNA depends on the ionic strength of the solution [6,12]. Various metal ions change the infectivity of tobacco mosaic virus RNA [25,47]. For example, it is found that the infectivity of the RNA of this virus correlates with the iron concentration in the preparations [25]. Nickel ions affect the infectivity of RNA more strongly than any of the other metal ions [47]. True, some authors [48] suggest that metal ions affect only the physical properties of tobacco mosaic virus RNA and not alter its infectivity.

The physical properties of RNA depend considerably on the presence of metal ions. Thus the sedimentation rate of solutions of nucleic acids [49] and their viscosity [50] decrease in the presence of Mn^{2+}, Ni^{2+}, Ca^{2+}, and Mg^{2+} ions. Na^+ and K^+ ions have a much weaker action than these and to bring about the same effect the concentration of alkali metal ions must be 2–3 orders of magnitude greater than the concentration of bivalent ions.

The melting point of the nucleic acids depends on the ionic surroundings [3,51,52]. On adding sodium chloride to DNA there is a linear relation between the melting point and the logarithm of the ionic strength of the solution. The increase in melting point with ionic strength is explained [3,51] by the stabilisation of the DNA with respect to the denaturing. It is suggested that the addition of electrolyte leads to screening of the charges in the DNA chains and this decreases the electrostatic repulsion forces between the charged phosphate groups, facilitating an increase in the rigidity of the structure.

Manganese, cobalt, zinc, and nickel behave like sodium chloride in raising the melting point of DNA, but copper, cadmium, and lead ions depress it [53,54]. Under conditions which facilitate the destruction of hydrogen bonds (heating the solutions of nucleic acids to 80° or dissolving them in 6 M urea — a reagent capable of destroying hydrogen bonds) such metal ions as Ni^{2+}, Mn^{2+}, Zn^{2+}, and Cr^{3+} decrease the optical density of RNA (raise the melting point), but alkali and alkaline earth metal ions hardly affect it. The conclusion was [7] that ions of the transition metals of the first period stabilise the structure of nucleic acids due to the formation of additional bonds between the metal and the bases of the acid. The intramolecular bonds formed with the metal are strong enough to withstand the destructive influence of a rise in temperature or the action of a concentrated solution of urea. With RNA the stabilising influence of the metal ions appears only on heating, when the hydrogen bonds are destroyed.

The change in the properties of the nucleic acids during the action on them of various metal ions is reversible. Katz [21] first drew attention to this ability by the reaction of DNA with mercury. He found that during reaction with $HgCl_2$ the DNA molecules become much smaller, but are restored by the action of reagents which bind mercury. On adding mercury salts to DNA there was a decrease in the characteristic viscosity of the DNA solution and in the spectral shift [20,21,55]. In combining with mercury the chacteristic viscosity and the position of the maximum in the DNA absorption spectrum acquired their original values. Reversible changes were also observed in studying sedimentation rate, scattering of light, optical rotatory

dispersion[56], and also the transforming ability[57] of DNA preparations†.

Hence no doubts remain about the complete reversibility of the reaction of DNA with mercury. This was confirmed by studying this reaction by methods sensitive with respect to the form and dimensions of DNA (viscosity, sedimentation rate, scattering of light), the peculiarities of the stereochemical configuration (optical rotatory dispersion), the presence of chromophoric groups and their relative orientation (absorption spectra in the near ultraviolet region). This was also confirmed by biological methods (transforming ability).

Such reversibility is characteristic for the reaction between tobacco mosaic virus RNA and mercury(II) chloride[56]. Unlike DNA, however, here the biological changes are not completely reversible. Thus Hg^{2+} ions completely deactivate the infectivity of tobacco mosaic virus RNA, but removal of these ions does not lead to complete reduction of the infectivity of RNA in comparison with the control.

Evidently the reaction DNA with Fe^{3+} ions, which was investigated by Gol'dshtein and Gerasimova[33,58], belongs to this type of reversible reaction. On introducing sodium pyrophosphate, which can bind iron, into a solution containing DNA and Fe^{3+} ions the ability of DNA to hydrolyse decreases.

The study of such reversible reactions, which are accompanied by a profound change in the physical properties of the nucleic acids, can evidently be of great importance in explaining the biological functions of the nucleic acids.

4. COMPOUNDS OF NUCLEIC ACIDS WITH METALS

Only a few compounds of the nucleic acids with metals have been isolated in the individual state. These compounds have mainly been investigated with the aim of finding methods for purifying DNA preparations. We will examine the method of obtaining them in somewhat greater detail.

As long ago as 1924 Hammarsten[59] observed that salts of lanthanum and iron(III) precipitate DNA from solution. The precipitation is maximal at pH 2.5–4. It was shown that the lanthanum nucleate compound has a very low solubility. This observation was confirmed later[60,61]. Stern and Steinberg[62] isolated and analysed compounds of DNA with lanthanum, neodymium, praseodymium, samarium, and yttrium, by adding the metal chloride solution to DNA solution, filtering off the fibrous precipitate, and thoroughly washing it with water, then alcohol, and drying in air. The dry products resembled asbestos fibres and had the colour characteristic of the rare-earth element. Suspensions of these compounds in glycerol had a marked absorption of light in the visible region of the spectrum. For the neodymium nucleato-complex the maxima of the absorption bands were at 510–512, 520–525, 570–590 mμ, and those for the praseodymium nucleato-complex were at 440–450, 465–470, and 475–480 mμ. The bands were clearly displaced relative to the bands for solutions of the pure rare-earth chlorides. The nucleate bands were much broader and less sharp than those for the chlorides. The solubility of the compounds was very low; for example, in the filtrate after separation of the neodymium nucleate from an aqueous suspension neodymium could not be detected spectrophotometrically by its absorption at 790 mμ or nucleic acid at 260 mμ. Ultimate analysis of the products showed that they contained 10.5 % neodymium and 11.1% lanthanum respectively.

The reaction between the lanthanide chlorides and sodium nucleate follows the equation[62]:

$$Ln^{3+} + 3\,DNA^- \rightleftarrows Ln(DNA)_3$$

where Ln is the lanthanide and DNA^- is the anion of sodium desoxyribonucleate.

The phosphate groups of the polynucleotide chain are ~ 6 Å from one another. The combination of one atom of rare-earth element with three phosphate residues is explained[62] by the formation of a sharply convolute polynucleotide tangle from one two-chain DNA spiral with the lanthanide ion in its centre. It was also suggested[62] that lanthanum ions can connect phosphate groups of neighbouring nucleotide chains, forming a network of filaments of different DNA molecules cemented to one another. The concentration of the lanthanide in such a complex should be 14%, but, as mentioned above for lanthanum and neodymium, the lanthanide concentration found did not exceed 11%. This is still unexplained.

The stoichiometry of the complex formation of metals with DNA was determined conductimetrically[63,64]. On the conductimetric curves for the titration of DNA with magnesium, manganese, barium, and calcium ions there are breaks corresponding to the stoichiometric ratio of one equivalent of metal ion : one of nucleotide. The position of the breaks is independent of the degree of denaturing of DNA and of the initial concentrations of the solutions.

As, however, such a ratio is not always[65,66] attained, additional proofs of the simple stoichiometry of the complexes were made[67,68]. Conductimetric titrations were made of synthetic polynucleotides: polyadenylic (poly-A) and polyuridilic (poly-U) acids, which contain only one base. These acids are capable of reacting with one another (this ability depends greatly on the nature and concentration of the metal ions present in the solution[69-71]). As a result of the reaction, the two single-chain acids form the double-chain acid poly-AU, which has properties reminiscent of those of DNA[70,72,73]. It has been shown that the titration curves of the two polymers and poly-AU are similar and reminiscent of the titration curves of DNA with magnesium ions and with manganese ions. The break on the titration curves (when a large number of points was taken during the titration) corresponded to the addition of 1 equiv. cation per 1 mole polymer phosphate. This ratio was the same whether native or denaturated DNA was titrated[74].

The composition of complexes of uranyl with DNA was also determined graphically[75]. The equilibrium concentration of uranyl ions in the solution after precipitation of the uranyl–DNA complex was plotted on the graph against the total concentration of uranyl ion in the initial solution. The approximate composition of the complex was determined from the break on the curve and it was shown that the stoichiometry of the complexes formed changes with the pH and the uranyl ion concentration, as Table 1 shows[75].

† Transforming ability is the name given to the ability of DNA isolated from one strain of bacteria to transmit definite characteristics, distinctive to the given progeny, for example, resistance to a certain poison, to another strain of bacteria. Transforming activity is inherent only in the native form of DNA. This index can be used as an experimental quantitative characteristic of the depth of denaturing and renaturing of DNA (Ref. 1, p. 269).

TABLE 1. Stoichiometry of the complex formation of uranyl with DNA as a function of pH and uranyl ion concentration. The DNA concentration has been recalculated per nucleotide link or per phosphorus of the nucleotide.

Experiments made at constant DNA concentrations ($\sim 4-6\times10^{-6}$ M) and variable pH		Experiments at constant pH ($\sim$3.5) and variable uranyl ion concentrations	
pH	UO_2^{2+}/P molar ratio	UO_2^{2+} concentration, M	UO_2^{2+}/P molar ratio
2.3	0.34	$1\cdot10^{-2}$	0.7
3.6	0.49	$4.8\cdot10^{-3}$	1.3
3.7	0.53	$6\cdot10^{-3}$	1.5
4.8	1.72		
5.8	2.42		

Probably this behaviour can be explained by the ability of the metal to form a compound not with a definite functional group of the DNA but, depending on the conditions, with different groups: phosphate, amino-, and enol.

The change in the stoichiometry of the metal–nucleic acid complexes with the pH and metal concentration was also observed in studying complex formation of Co^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, and Mn^{2+} ions with RNA and DNA by the equilibrium dialysis and isotope dilution methods[76]. On increasing the metal ion concentration the bonding of metal increases. Table 2 gives the results of determining the value of the "degree of bonding" at different pH and constant metal ion concentration, expressed in the number of metal atoms per atom of DNA phosphorus.

The complex formation of different metals with DNA has also been studied by the NMR method[77]. The paramagnetic metal ions in aqueous solution shorten the time of spin-lattice relaxation of the water protons. The relaxation time for protons in aqueous solution containing paramagnetic metal ions depends not only on the metal concentration but also on its chemical environment. It is known that there is greater effectiveness in shortening the relaxation time when there are small ions or molecules in the environment than when the metal is inside a large molecule.

TABLE 2. Bonding of the doubly-charged ions of certain metals with DNA at various pH and constant metal ion concentrations. Concentrations: metal ion 10^{-2} g litre^{-1}; Ca^{2+} 2.1×10^{-2} g litre^{-1}; DNA 10^{-5} g.*

pH	No. of metal ions per RNA phosphorus atom					No. of metal ions per DNA phosphorus atom				
	Co^{2+}	Zn^{2+}	Ca^{2+}	Mn^{2+}	Mg^{2+}	Co^{2+}	Zn^{2+}	Ca^{2+}	Mn^{2+}	Mg^{2+}
3.6	0.140	0.056	0.058	0.035	0.032	0.028	0.020	0.029	0.018	0.029
4.0	0.144	0.078	0.068	0.042	0.045	0.036	0.026	0.040	0.026	0.035
4.4	0.137	0.090	0.062	0.049	0.045	0.037	0.028	0.043	0.026	0.038
4.8	0.129	0.095	0.059	0.047	0.051	0.039	0.029	0.043	0.024	0.035
5.2	0.115	0.088	0.065	0.047	0.048	0.040	0.026	0.042	0.022	0.031
5.6	0.110	0.081	0.059	0.047	0.046	0.037	0.024	0.041	0.019	0.030
6.0	0.114	0.092	0.067	0.050	0.052	0.040	0.026	0.040	0.022	0.030
6.4	0.114	0.086	0.066	0.050	0.048	0.042	0.028	0.039	0.020	0.029
6.8	0.102	0.088	0.067	0.051	0.043	0.037	0.027	0.040	0.020	—
7.2	0.104	0.085	0.069	0.050	—	0.031	0.028	0.042	0.021	—
7.6	—	0.089	0.068	0.048	0.045	—	—	0.036	0.021	0.029
8.0	0.109	—	0.071	—	0.044	0.038	0.029	0.039	—	0.031
8.4	—	—	0.071	—	—	—	—	—	—	—
8.8	—	—	0.071	—	—	—	—	—	—	—

* These concentrations do not agree with those given in Table II of Ref. 76 (Ed. of Translation).

TABLE 3. Determination of the number of DNA parts available for absorption.

Metal ion	No. of metal ions arriving per 1 mg DNA	No. of equivalents of metal arriving per nucleotide
Mn^{2+}	$7\cdot10^{17}$	0.7
Cr^{3+}	$7\cdot10^{17}$	1.1
Fe^{3+}	$8\cdot10^{17}$	1.2

A theoretical appraisal was made of the decrease in relaxation time during the bonding of a metal ion with one or another part of the DNA molecule (by the parts of the linking DNA we mean the phosphate, amino-, and enol groups of the molecule) and the calculated quantities were compared with the experimental results obtained. On this basis the probable parts of the bonding DNA with various metals were determined and the "capacity" of the DNA molecule in relation to these metals. Table 3 gives these quantities.

As Table 3 shows, the same ratio is retained for complex formation for ions of iron and chromium: 1 equivalent of metal to 1 of nucleotide. Manganese ions do not obey this rule.

In studying the reaction of metal ions with tobacco mosaic virus RNA using labelled atoms (the radioactivity of a solution of a salt of the metal before reaction with RNA was compared with the radioactivity of a mixture of solutions of the metal salt and RNA after removal of the metal–RNA complex from it by centrifuging), it was found that the RNA bonds 0.5 mole calcium salt per nucleotide and $\sim$ 1 mole mercury or silver salt per nucleotide[78].

Despite the fact that the composition of the complexes formed by metals with nucleic acids often corresponds to simple stoichiometric ratios, it must be remembered that simple stoichiometry cannot be fulfilled on account of the possibility of complex formation by the metal with different functional groups of the nucleic acids.

5. STRUCTURE OF COMPLEXES OF METALS WITH NUCLEIC ACIDS

In studying the structure of compounds of the type mentioned the region of the metal–nucleic acid bond is usually determined. To identify the region, the reaction of the metals with native and denatured forms of DNA are often compared. When these reactions do not depend on the form of DNA, the bond between the acid and the metal is effected directly with the phosphate groups. When the reaction depends on the form of DNA, this is evidence of the formation of a bond between the metal and the purine or pyrimidine bases of the acid. In native DNA these bases, as already mentioned, are linked by hydrogen bonds, and consequently their reaction with metal ions is hampered

By use of conductimetric titration[63,64,74] it was found that magnesium, manganese, barium, and calcium ions behave similarly in relation to native and denatured DNA. The position and character of the breaks on titration curves of the acid by these ions are independent of the degree of denaturing and over a wide range of concentrations correspond to a definite stoichiometric ratio of DNA and metal ions. Consequently it can be assumed that these metal ions are connected with the phosphate groups of the DNA. This conclusion is also confirmed by the following facts[74].

It is known[79] that the dye Acridine Orange reacts only with the phosphate groups of nucleic acids in 1 : 1 ratio and that the conductimetric titration curves for DNA by this dye are analogous to the curves for the titration of DNA by Mg^{2+} or Ba^{2+} ions and also the curves for the titration of poly-A, poly-U, and poly-AU by these ions. Hence the reaction of these metal ions with the different polynucleotides is independent of the composition of the bases and is determined by the phosphate groups.

In studying the reaction of the same metal ions with nucleic acids by the equilibrium dialysis method[76] differences were also noted in the degrees of bonding for the same ion with different forms of DNA. The effect of magnesium and calcium ions on the fluorescence of the ring of adenine, adenosine, adenosine monophosphate, adenosine diphosphate, and adenosine triphosphate was also studied[80]. The maximal intensity of the fluorescence of these substances, observable at 395 mμ, changed in the sequence: adenosine < adenosine monophosphate < adenosine diphosphate, adenine < adenosine triphosphate. Magnesium and calcium ions lowered to an almost equal extent the fluorescence of adenosine triphosphate and adenosine diphosphate to the intensity of adenosine monophosphate and adenosine respectively. These results serve as yet another confirmation that magnesium and calcium ions are connected mainly with the phosphate moiety of the nucleotide and are not attached to the ring of the base.

Study of the effect of metal ions on the melting point of nucleic acids can also be used to determine the region of bonding. It is known[53,54] that Mn^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+} ions raise the melting point but Cu^{2+}, Cd^{2+}, and Pb^{2+} ions depress it. This is explained[53,54] by the fact that the metals of the first group are connected with the phosphate residues at the DNA surface, which prevents electrostatic repulsion of the negatively charged phosphate residues and stabilises the DNA molecule. The metals of the second of these groups are bound to the purine or pyrimidine bases inside the spiral, in the sites of the hydrogen bonds, and destabilise the DNA molecule.

By use of the NMR method[77] it was also found that Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} ions are most probably bound to the phosphate groups and not the nitrogenous bases of the DNA, but Fe^{3+} ions are linked with the nitrogenous bases. As for copper ions, they bring about the aggregation of the DNA molecules and, it is thought[77], are connected with the outer phosphate parts of the DNA. However, in the EPR spectra of DNA solutions treated with Cu^{2+} ions signals are observed which are explained[81] by the formation of a bond between the copper ions and the bases of the DNA.

The reaction of uranyl ion with DNA[75] apparently occurs at the phosphate groups. In investigating the complex-forming ability of several phosphates in relation to the uranyl ion it was found that the molar ratio of uranyl to phosphorus increases with the number of phosphate groups in linear phosphate polymers. Undoubtedly DNA can be included among these polymers. Direct proof of the connection of the uranyl ion and the phosphate groups is given by the infrared absorption spectra of DNA solutions in the presence and absence of uranyl salts[75].

Fig. 4 shows the infrared absorption spectrum of DNA. The 900–1300 cm^{-1} band belongs[82] to the vibrations inside the phosphate groups and sugars, the strong 1500–1600 cm^{-1} band to the vibrations of the >C=N–, >C=O, and >C=C groups of the nitrogenous bases, and the 3000–3500 cm^{-1} band to the vibrations of the amino- and hydroxyl groups in the sites of the hydrogen bonds[83].

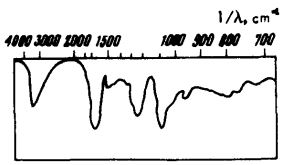


Fig. 4. Infrared spectrum of calf thymus DNA (sodium salt).

During complex formation with the uranyl ion some shifts in the position of the bands were observed only in the region from 900 to 1300 cm^{-1}. However, it must be noted that in comparing the infrared spectrum of DNA with that of the DNA–iron complex[84], only displacements of the bands of the stretching vibrations of the phosphate ester groups are observed and not a displacement in the region of the vibrations of the >C=N–, >C=O, and >C=C< groups of the bases. Moreover, it was found by differential spectrophotometry in the ultravoilet region (spectra of solutions of the metal–DNA complex recorded in relation to solutions of the free ligand and metal[85]) that iron ions also react with the DNA bases[84]. Similarly, in comparing the infrared spectra of adenosine triphosphate (ATP) and of copper–ATP complexes a displacement in the regions of the vibrations of the chromophoric groups of the bases was not observed. A displacement of the ATP absorption band into the ultraviolet region is observed in the differential spectrum and can be explained only by the reaction of copper ions with the bases[85]. The possibility of coordination between copper ions and purine components of the DNA has also been established in studying the effect of nucleic acids and their components on the oxidation of ascorbic acid, which is catalysed by copper ions[86].

Apparently infrared spectroscopy has still not unambiguously settled the problem of the locations of the bonds between the metals and nucleic acids.

Studying the absorption spectrum of DNA solutions in the near ultraviolet region in the presence of ions of various metals also allows conclusions to be drawn about the locations of the bonding of metals to DNA. It is known[87] that additions of Mg^{2+}, Ca^{2+}, and Mn^{2+} ions do not change the position of the bands in the DNA absorption spectrum, whereas Hg^{2+} or Ag^{+} ions displace the absorption band (Fig. 5)[55].

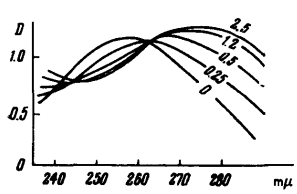
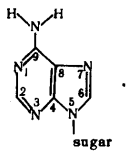


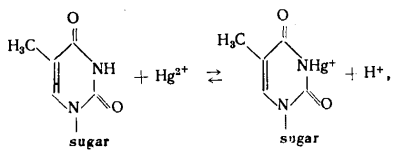
Fig. 5. Effect of $HgCl_2$ on the absorption spectrum of solutions of calf thymus DNA in 0.1 M $NaClO_4$, pH 5.6–5.7 at various ratios of moles $HgCl_2$ to moles DNA phosphorus (r). Values of r are shown on the curves.

In this connection it is suggested[55,88] that mercury and silver ions bond with DNA through the nitrogenous bases. Depending on the value of r (the ratio $[Hg^{2+}]/[PO_4^-]$) this reaction proceeds either with or without release of hydrogen ions[55,88]. This is explained by the attachment of the metal ions to different DNA bases, during which the hydrogen bond between the chains can be destroyed or remain unchanged.

When complex formation is not accompanied by the liberation of hydrogen ions it is suggested[55] that the metal ion is attached to the electron pair of the 7-N or 3-N of the purines adenosine or guanosine. The hydrogen bonds are not destroyed during this.

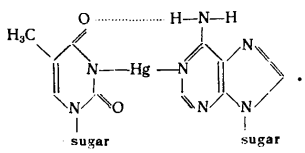


When hydrogen ions are released it can be assumed that there is a reaction of the type:



accompanied by the rupture of the hydrogen bonds.

Considering the reaction between mercuric ions and DNA, Katz[89,90] proposes that in the region $0 \leq r \leq 0.5$ compounds are formed in which the mercury play the part of an intermediate bridge between two coils of the DNA double spiral, the hydrogen bonds of which are not completely destroyed:



Such a complex is a two-filament polynucleotide in which almost all the bases of one filament are connected to the bases of the other by bridges of mercury atoms. The composition of such a complex corresponds to a mercury-nucleotide ratio of 1 : 2.

At $r \geq 0.5$ the filaments are separated, with formation of complexes of 1 : 1 composition by the reactions

$$\text{chain–base } a\text{–}Hg^{II}\text{–base } b\text{–chain} + Hg^{II} \rightleftharpoons$$
$$\rightleftharpoons \text{chain–base } aHg^{II} + \text{chain–base } bHg^{II}.$$

A conclusion about the bonds between metals and the nucleic acid bases can be drawn from a study of the ultravoilet spectra only when there is a marked displacement of the maxima of the absorption bands of the nucleic acids as a result of the action of the metal, as happens for silver and mercury ions; when this is not so, it is necessary to study differential spectra in the ultraviolet region[85].

There are grounds for assuming that all the above mentioned methods of determining the structure of the metal–DNA complex do not give unambiguous results. It would appear, undoubtedly, that alkaline earth metal ions are bonded with DNA through phosphate groups. However, in using the equilibrium dialysis method[65] it was shown that Mg^{2+} ions act differently in relation to denatured and native forms of DNA. In this connection there is the possibility[54,91-93] that Mg^{2+} is bonded with the bases, mainly the purines, which have a structure reminiscent of quinolin-8-ol, whose great affinity for magnesium is well known.

It has been shown[93] that the addition of Mg^{2+} or Ca^{2+} to unionised nucleoside triphosphates brings about the same spectral shift as their neutralisation with OH^-. Probably, protons are displaced from the ring in both instances.

It is suggested[93] that because of the spiral configuration of the nucleoside triphosphate, the formation of bonds between magnesium and two parts of the nucleotide — the phosphate group and base — is possible.

Conformational analysis made with Steward models of atoms for the iron–nucleotide system[94] also confirm the possibility of bonds being formed simultaneously between metal, phosphate group, and base.

It is quite probable that the metal ions form bonds not with individual atoms of the rings of the bases but with the entire molecule of the base as a whole; this involves the overlap of the molecular orbitals of the base and the orbitals of the metal. It can be assumed that sometimes compounds are formed of the type of complexes with charge transfer using both the orbitals of the metal and molecular orbitals of the base and the d orbitals of the phosphorus atoms.

6. STABILITY OF COMPLEXES OF METALS WITH DNA

Some idea of the stability of the compounds formed can be obtained by comparing their association constants. Table 4 gives the values of the known association constants of complexes of DNA with various metals and shows that there are no sharp differences in the constants for different metals.

The example of silver complexes (Table 5) shows that the origin of the DNA has little effect on the association constants.

In calculating the constants it was assumed that the formation of a bond in each portion is independent of the occupation or unoccupation of the other parts. In one study[95] it was assumed that the composition of the complex corresponds to a metal : nucleotide ratio of 1 : 1. In the other studies the number of combining parts of the nucleic acid and the association constants were determined by a graphical method, the general principles of which for polyelectrolytes have been described[96].

TABLE 4. Association constants of complexes of metals with DNA.

Complex of DNA with the metal ion	Method of determining the equilibrium concentration of the metal	pH	Ionic strength	Association constant	Reference
Mg^{2+}	equilibrium dialysis		0.2	$2.8 \cdot 10^2$	65
Mg^{2+}	metal-indicator (Eriochrome T)	10	0.002	$2 \cdot 10^5$	97
UO_2^{2+}	titration with cyanoferrate(II)	3 5	0	$8 \cdot 10^6$	75
Ag^+	potentiometric	5.6	0.1	k_1 $2.4 \cdot 10^6$	88
Ag^+	potentiometric	5.6	0.1	k_2 $3.4 \cdot 10^5$	88
Fe^{3+}	kinetic	3.1	~0	$1.3 \cdot 10^5$	95

TABLE 5. Association constants of complexes of silver with DNA from various sources [88].

Specimen of DNA	k_1 $0<r<0.2$	k_2 $0.2<r<0.5$
Calf thymus DNA 1 native	$2.1\cdot10^6$	$4.1\cdot10^4$
Calf thymus DNA 2 native	$2.2\cdot10^6$	$7.4\cdot10^4$
Calf thymus DNA 2 denatured	$4.2\cdot10^6$	$1.3\cdot10^5$
E. Coli	$2.2\cdot10^6$	$5.7\cdot10^4$
M. Lysodeikticus	$3.1\cdot10^6$	$2.4\cdot10^5$

It has been shown [95] for the iron–DNA complex that the equilibrium constant is almost independent of temperature and consequently the heat of the reaction is small. On this basis the entropy of complex formation has been calculated to be ~ 23 e.u. The positive change in entropy is due to the dehydration of the ions during complex formation.

As stated above, metal ions, especially those of the transition metals, can be coordinated simultaneously with many functional groups, and for each group the stability constant will be different. Therefore association constants quoted are often mean values.

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For a long time it was thought that the occurrence of metals in nucleic acids was due to accidental contamination. From this review it is clear that metals can react with nucleic acids and the compounds formed often exhibit properties differing from those of the original acids.

One of the most interesting properties which characterise the complex formation between nucleic acids and metals is the reversibility of changes in the structure of the nucleic acids brought about by coordination with the metals. It is thought that the reversibility is a general feature of the behaviour of double-filament, polynucleotides consisting of two filaments bound by hydrogen bonds [98]. At high metal concentrations this reaction takes place up to complete separation of the filaments of the spiral of the DNA and the formation of 1 : 1 complexes. This form of separation of the chains is different from thermal separation in that chemical damage to the structural entity of the DNA (liberation of purines, breaking of phosphate ester bonds, etc.) is excluded completely.

Study of the absorption spectra of nucleic acids in the presence of $HgCl_2$ showed [56] that, in contrast to DNA, RNA forms a complex at $r > 1.0$. The same phenomenon was observed in experiments with DNA denatured by heating [55]. It is therefore proposed [56] that the reaction with $HgCl_2$ can also be used for finding differences between single-filament and two-filament polynucleotides.

Only a few metal ions (Hg^{2+}, Ag^+, and apparently Fe^{3+}) have yet been found which are capable of such reversible action towards nucleic acids. Probably a search for reversible reactions for other metal ions can give interesting results.

A necessary prerequisite for such investigations should be the determination of the regions of bonding of the metals with the nucleic acids. As the above review shows, there is no incontrovertible proof of a bond between the metal and any specified sections.

We see the importance of studying the complex formation of nucleic acids with metals also in the possibility of obtaining especially pure preparations of these substances. For this purpose quantitative characterisation of the complex formation is necessary — information about the association constants of the corresponding complexes. As we have seen, these data are extremely fragmentary. Moreover, we need further confirmation and reasons for the fact that the association constants for such different metals ions as Mg^{2+}, UO_2^{2+}, Ag^+, and Fe^{3+} are very similar.

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SPECTROSCOPIC STUDIES ON REVERSIBLE REACTIONS IN COMPOUNDS OF THE PORPHIN SERIES

A.N. Sidorov

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INTRODUCTION

One has merely to list only a few examples of compounds of the porphin series to show clearly, without further comment, the urgent need for a comprehensive study of the compounds of this series, from the simplest onwards. Compounds of this series include chlorophyll — the green pigment of the photosynthesising mechanism in plants, haem — the red pigment of blood, responsible in haemoglobin for the transport of oxygen and carbon dioxide in the circulatory system, the prosthetic groups of cytochromes — biological catalysts controlling the processes of tissue respiration, and phthalocyanines — synthetic compounds which have found extensive application as dyestuffs.

The structure and physicochemical properties of chlorophyll were first studied at the beginning of last century, but it was only in the nineteen-twenties and -thirties that the work of several generations of Russian and other scientists led to the first synthesis of the simplest porphin derivatives and the determination of the structural formulae of chlorophyll and haem†. In the post-war years the attention of many research workers was drawn to the specific ability of compounds of the porphin series to undergo reversible reactions. These reactions are undoubtedly of particular scientific interest, since they characterise or even determine the biological activity of the pigments. Considerable progress was made in this field as a result of the application of new physical methods, particularly spectroscopic methods: electronic and vibrational absorption spectra, luminescence spectra, electron spin resonance (ESR) spectra, and nuclear magnetic resonance (NMR) spectra. Valuable experimental material has now accumulated, but is is difficult to see one's way through the vast quantity of unrelated data. Thus at the present time, in addition to a continuation of experimental work, there is a need for systematisation and summary of published results, and this is the purpose of the present review. We shall examine the interactions of molecules of the porphin series with the medium and also some of their photochemical reactions. The reversible reactions involved in the reduction and oxidation of chlorophyll, and its photosensitising action, have been studied in detail in reviews by Krasnovskii[8], Evstigneev[9], and Livingston[10] and in a monograph by Rabinowitch[1], so that we shall not deal with these topics. In view of their specific character and direct relationship to the function of haemoglobin, the properties of the iron-containing complexes form a separate chapter of science and will be discussed only in the examination of the general properties of metal derivatives of the porphin series. The purely spectroscopic characteristics of compounds of the porphin series have been described in a review by Gurinovich et al.[11] and their physicochemical properties have been described in papers by Phillips[12,13] and Falk[14].

† The history of the discovery and study of chlorophyll, haem, and other porphin derivatives is described in more detail in a number of monographs[1-7].

I. NOMENCLATURE AND MOLECULAR STRUCTURE OF COMPOUNDS OF THE PORPHIN SERIES

The skeleton of the porphin molecule (I, II) is made up of four pyrrole rings joined to one another by methine bridges to form a closed cyclic system with conjugation throughout the entire ring. Depending on the arrangement of the two central H atoms, two isomers of porphin are possible in principle, with *trans*- or *cis*-arrangement of the imine NH bonds.

Porphin derivatives with substituents in positions 1–8 are called porphyrins. For example, etioporphyrin I is 2,4,6,8-tetraethyl-1,3,5,7-tetramethyl-porphin, and protoporphyrin IX is 1,3,5,8-tetramethyl-2,4-divinylporphin--6,7-dipropionic acid. It is possible to distinguish four isomers of etioporphyrin and 15 isomers of protoporphyrin, depending on the mutual arrangement of the substituents. The isomers are denoted by Roman numerals (etioporphyrin I, etioporphyrin **II**, etc.). The nomenclature of the porphyrins, methods for their preparation, and properties have been described in detail in a monograph by Fischer[6] and in a review by Phillips[13].

The H atoms of the methine bridges of the porphin molecule, like the H atoms of the pyrrole rings, can also be replaced. Thus for example $\alpha\beta\gamma\delta$-tetraphenylporphin and $\alpha\beta\gamma\delta$-tetramethylporphin (or simply tetraphenylporphin and tetramethylporphin) are known.

The porphin derivative in which a benzene ring is fused to each pyrrole ring is called **tetra**benzoporphin (III).

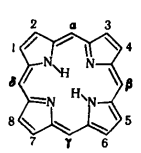
Hydrogenation of one or two of **the pyr**role rings of the porphin molecule gives dihydroporphin or chlorin (IV) and tetrahydroporphin or bacteriochlorin (V) respectively. Chlorin and bacteriochlorin also form derivatives corresponding to those of porphin. It is suggested that the hydrogenated pyrrole rings in the molecules of tetraphenylbacteriochlorin[15] and octaethylbacteriochlorin[16] may be situated in either the *trans*-position or the *cis*-position relative to one another (V, VI). It may be assumed that the same possibility exists for other bacteriochlorin derivatives‡.

A unique position among porphin derivatives is occupied by the azaporphins — compounds in which some or all of the methine bridges are replaced by nitrogen atoms. Derivatives of monoaza-, diaza, triaza, and tetra-azaporphin(VII) are known. Tetrabenzotetraazaporphin is usually called phthalocyanine (VIII).

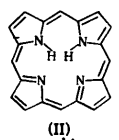
Porphin and all its derivatives can form complexes with various metals, by replacement of the H atoms of the imine groups in the centre of the molecule. The complex

‡ The term "bacteriochlorin" is obtained by analogy with the term "bacteriochlorophyll" (the tetrahydro-derivative of porphin with the *trans*-arrangement of the hydrogenated pyrrole rings). Up to the present, therefore, this term has been applied in the literature only to the *trans*-isomers of tetrahydroporphin and its derivatives. Since a terminology for the hydrogenated derivatives of porphin has not yet been established, however, it will be convenient to extend this term to the *cis*-isomers.

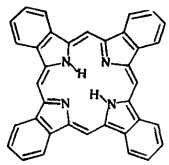
formed by porphin with a bivalent metal (M-porphin) is represented by formula (IX). When porphin derivatives form complexes with tervalent or quadrivalent metals, one or two anions respectively, usually OH^-, HSO_4^-, Br^-, or Cl^-, are attached to the metal atom at ring angles to the plane of the molecule.



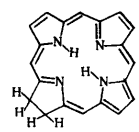
(I) porphin, *trans*-isomer



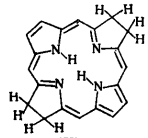
(II) porphin, *cis*-isomer



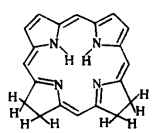
(III) tetrabenzoporphin



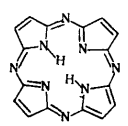
(IV) chlorin



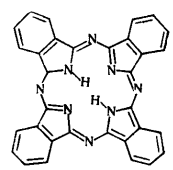
(V) bacteriochlorin *trans*-isomer



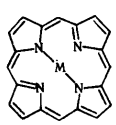
(VI) bacteriochlorin *cis*-isomer



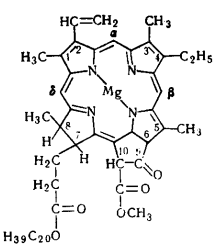
(VII) tetra-azaporphin



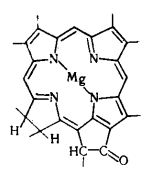
(VIII) phthalocyanine



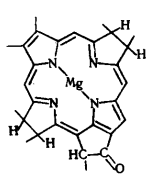
(IX) M-porphin



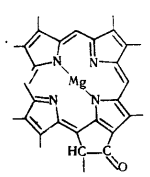
(X, *a*) chlorophyll *a*



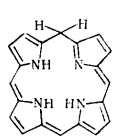
(X) chlorophyll



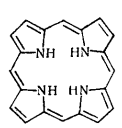
(XI) bacteriochlorophyll



(XII) protochlorophyll



(XIII) phlorin



(XIV) isophlorin

Most of the biologically important pigments among the porphin derivatives are complexes with metals. Thus haem is Fe^{II}-protoporphyrin IX; haemin (chlorohaemin) is $Fe^{III}Cl$-protoporphyrin IX; and haematin is $Fe^{III}OH$-protoporphyrin IX. Chlorophyll, bacteriochlorophyll, and protochlorophyll are magnesium-containing derivatives of chlorin, bacteriochlorin, and porphyrin respectively. The skeleton of the molecular structure of these pigments is given by formulae (X), (XI), and (XII); the substituents in all are the same [see formula (X,*a*)]. An important characteristic of the molecular structure of chlorophyll, bacteriochlorophyll, and protochlorophyll is the presence of the so-called cyclopentanone ring joined to the tetrapyrrole skeleton of the molecule via the C atoms in positions 6 and γ. There exist analogues of chlorophyll without a metal atom in the centre of the molecule (pheophytin) and analogues in which the Mg atom is replaced by an atom of another metal (Cu-pheophytin, Ni-pheophytin, etc.). Methylchlorophyllide is a chlorophyll analogue with a methyl group in place of the $C_{20}H_{39}$ group in position 7.

Woodward [17] recently suggested that porphyrins may be hydrogenated not only in the pyrrole rings but also at the methine bridges and central nitrogen atoms with the formation of the so-called phlorins (XIII) and isophlorins (XIV). Strictly speaking, phlorin cannot be included among the compounds of the porphin series, since these are characterised by the presence of a closed ring of conjugated bonds.

The presence of the cyclic system of conjugated bonds in the molecules of porphin and its derivatives is the factor which determines the characteristic features and properties of these molecules. Measurements of the limiting luminescence polarisation of symmetrically substituted M-porphin derivatives (where M is a bivalent metal) have led to the conclusion that the molecules of these compounds belong to a point group with symmetry D_{4h}. This means that, as a result of the delocalisation of the π electrons in the system of conjugated bonds, all four pyrrole rings and all four M–N bonds and other symmetrically arranged atoms and bonds become equivalent [11]. In particular, the concept of "semi-isolated" double bonds [1] in the porphyrin molecules becomes meaningless. In the case of non-symmetrical derivatives of porphin (chlorins, bacteriochlorins, and unsymmetrically-substituted porphyrins) the equivalence of the atoms and bonds breaks down to some extent, leading to a change in some of the properties of the compounds. In this case also, however, the degree of delocalisation of the π electrons in the conjugated system is fairly high and it is possible to speak of the relative equivalence of the M–N bonds and non-hydrogenated pyrrole rings.

II. ISOMERISM AND TAUTOMERIC CHANGES

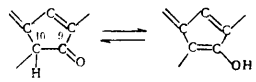
Let us examine first the problem of the isomerism of the imino-groups in the porphin molecule. As noted above, isomers of porphin with *cis*- and *trans*-arrangement of the imino-groups (I) and (II) are possible in principle. The point group symmetry of the molecule of the *trans*-isomer is D_{2h}, and that of the molecule of the *cis*-isomer is C_{2v}. According to the selection rules, for molecules with symmetry D_{2h} the range of the stretching vibrations of the NH bonds should contain only one absorption band, but for symmetry C_{2v} two bands are possible [18]. Spectroscopic measurements have shown that porphin [18] and all its derivatives, including chlorin, bacteriochlorin [19], and phthalocyanine [20], have only one band in this range, corresponding to *trans*-arrangement of the imino-groups. Measurements of the limiting luminescence polarisation of porphin and its symmetrically substituted derivatives [11] confirmed that the molecules of these compounds belong to the point group with symmetry D_{2h}.

It would, however, be premature to conclude that the possibility of *cis*-arrangement of the imino-groups in molecules of the porphin series is excluded. Spectroscopic measurements in the infrared range have up to the present been mainly qualitative; they do not exclude the possibility that the absorption bands are superimposed and hence that the interpretation of the results is ambiguous. This possibility is confirmed by the infrared spectrum of pheophytin *a*. In this spectrum the range of stretching vibrations of the NH bonds contains an absorption band with three maxima, which can be assigned to isomers of the pigment with different arrangements of the imino-groups [21].

The conclusion that tautomeric transformations of the *trans*- and *cis*-isomers of porphin compounds into one another are possible was reached by Dorough and Shen [22], who observed reversible changes in the fluorescence and

absorption spectra of solutions of tetraphenylporphin and tetraphenylchlorin with decrease in temperature from 20° to -196°. The spectra of metal derivatives of these pigments did not show similar changes. This phenomenon was attributed to displacement of the dynamic equilibrium between tautomers with change in temperature. This explanation requires verification, however, since it is held that the change in the spectroscopic characteristics of tetrapyrrole pigments with decrease in temperature is due not to tautomeric changes in the molecules but to resolution of the vibrational structure of electronic transitions [11]. Further progress towards a solution of the problem of isomerism and tautomeric changes in porphin compounds requires new studies, particularly in infrared and NMR spectroscopy.

According to data obtained by many workers [1], the Molisch phase-test reaction, which involves the production of a brown colour in an ethereal solution of chlorophyll when alcoholic alkali is added, begins by alkali-induced enolisation of the carbonyl group in position 9:


(XV).

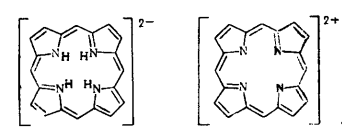
It is not excluded that keto–enol tautomeric changes also take place in chlorophyll molecules in the absence of alkali. In the determination of the proportion of enolised chlorophyll molecules under different conditions, considerable reliance is placed on infrared spectroscopy. It is suggested that the intensity of the absorption bands corresponding to the vibrations of the OH, C=C, and C=O bonds may provide a reliable measure of the quantity of keto and enol forms of chlorophyll molecules. The difficulties of interpretation of the infrared spectra, however, have led to contradictory views on the data obtained [23-28]. It is found that the presence of absorption bands in the spectrum of chlorophyll in the range corresponding to the stretching vibrations of the OH groups does not provide adequate proof of the existence of enolised molecules, since in this range radiation is also absorbed by molecules of water, which is associated with the chlorophyll and is difficult to remove [29]. The absorption bands of chlorophyll in the range of vibrations of the C=C and C=O bonds (1500–1750 cm^{-1}) can be interpreted in different ways [23-28,30] and therefore cannot provide a sufficient basis for concluding that keto–enol tautomerism occurs in chlorophyll. In this connection it must be admitted that conclusions regarding the presence of an appreciable quantity of enolised chlorophyll molecules in various solvents, reached merely on the basis of spectro-analytical measurements in the infrared range [23-25,30,31], have insufficient foundation. Recently, study of isotope exchange between chlorophyll and CD_3OD in chloroform has shown that the rate of replacement of the H atom in position 10 by deuterium is relatively low. Without excluding the possibility, in principle, of the existence of enolised chlorophyll molecules, this experiment shows that the proportion of such molecules under the conditions of the experiment is small and cannot determine to any significant extent the absorption spectrum of the pigment in the infrared range [26,32,33].

III. MOLECULAR COMPOUNDS

Let us examine the reaction of molecules of porphin compounds with one another or with the molecules of the medium, leading to the formation of association and molecular complexes with a significant change in the properties of the pigments, including their spectroscopic characteristics. The ability of molecules of the porphin series to form complexes with the molecules of the medium is by no means a distinctive feature of this series but is of exceptional biochemical importance. This property is decisive in enabling haemoglobin to perform its function as oxygen carrier. The reaction of chlorophyll molecules with the molecules of the medium ensures that the interacting components are prepared for the fundamental photochemical step.

1. Compounds with an ionic structure. In the extreme case of strong interactions ionisation of the pigment molecule takes place. Porphyrins are amphoteric compounds [12,13]. All four nitrogen atoms of the porphyrin molecule are basic centres and may act as proton acceptors. The imino-groups (NH) are capable of losing protons under certain conditions, that is, of acting as acidic centres. If the neutral porphin molecule is denoted by $H_2\Pi$, six ionic forms are possible in principle: reaction with strong bases may lead to the formation of $(H\Pi)^-$ and Π^{2-} ions and reaction with acids to the formation of the ions $(H_3\Pi)^+$, $(H_4\Pi)^{2+}$, $(H_5\Pi)^{3+}$, and $(H_6\Pi)^{4+}$. Divalent anionic and cationic forms of some porphyrins have been isolated in the form [12] of salts $Na_2^+\Pi^{2-}$ and $(H_4\Pi)^{2+}Cl_2^-$. In particular, tetraphenylporphin and tetraphenylchlorin dihydrochlorides are formed when the original pigments are kept in gaseous HCl [34,35]. This method can apparently also be used to prepare the hydrochlorides of other porphin derivatives.

Measurements of the luminescence polarisation show that the divalent porphyrin cation $(H_4\Pi)^{2+}$, like the metal–porphin molecule, has the point group symmetry D_{4h}. From this it follows that the excess of charge in the divalent ion is distributed uniformly throughout the cyclic system of conjugated bonds and that all four pyrrole rings are equivalent [11]. The position and width of the absorption bands in the region of the stretching vibrations of the NH bonds in the infrared spectra of tetraphenylporphin and tetraphenylchlorin dihydrochlorides [34,35] show [36] that these bonds have ionic character $(NH)^+$. This means that the excess of charge in the structure of the divalent porphyrin and chlorin cations, although included in the cyclic system of conjugated bonds, is chiefly concentrated close to the NH bonds and is distributed uniformly between them. On the basis of these ideas, the structure of the cation can be represented by formula (XVI). The analogous formula (XVII) can be used to describe the structure of the divalent anion:



(XVI) porphin divalent cation (XVII) porphin divalent anion

Singly-charged porphyrin ions have as yet been observed only in exceptional cases. Thus it is suggested that the absorption spectrum of the monovalent protoporphyrin cation can be observed in the presence of certain aqueous detergents [37]. The singly-charged porphyrin ions are evidently short-lived intermediate products which are rapidly converted into doubly-charged ions. This is apparently due to the instability of structures in which one of the central N atoms is not equivalent to the others (in the case of the monovalent anion it form an imino-group, unlike

the other three N atoms, and in the case of the monovalent cation it has no H atom whereas the other N atoms form imino-groups). In the reaction between acids and chlorins in which the equivalence of the pyrrole rings has been broken down by hydrogenation of one of the lateral double bonds both divalent and monovalent cations can be observed spectroscopically [11].

The ionic forms of metal derivatives of the porphin series have been less extensively studied. On contact with metallic sodium in absolute dry tetrahydrofuran in a vacuum, Mg-phthalocyanine is converted into the anionic form [38,39]. The number of electrons attached to the pigment molecule in the process is still unknown. On contact with oxygen, the Mg-phthalocyanine anions are reversibly converted into the original pigment. It was recently found that the reaction of Zn-tetraphenylporphin with certain organosodium compounds leads to the formation of salts of the monovalent and divalent anions of the pigment. The salts $Na^+(ZnTPP)^-$ and $Na_2^+(ZnTPP)^{2-}$ were isolated in pure form [40]. As in the case of porphyrins containing no metals, the excess of charge in the Mg-phthalocyanine and Zn--tetraphenylporphin ions is apparently distributed uniformly throughout the cyclic system of conjugated bonds.

The metal derivatives of compounds of the porphin series can be divided into two groups according to the nature of their reaction with acids. The first group consists of those derivatives in which this reaction leads to replacement of the central metal atom by two H atoms, that is to irreversible conversion of the metal-containing complex into pigment containing no metal. The second group consists of metal derivatives which are fairly stable towards acids but which react to form cations in which the central metal atom is preserved. The stability towards acids depends chiefly on the stability of the bond formed by the metal atom with the ligand. This stability decreases in the order [12]:

$$Pt^{II} > Pd^{II} > Ni^{II} > Co^{II} > Ag^{II} > Cu^{II} > Zn^{II} > Mg^{II} > Cd^{II} > Sn^{II} > Li > Na > K > Ag.$$

The stability towards acids also depends on the structure of the pigment molecule and on the conditions under which the reaction with acids takes place. Thus when sublimed layers of Zn-phthalocyanine and Zn-tetraphenylporphin are brought into contact with gaseous HCl, the former is stable [41] whereas the latter is converted into the hydrochloride of tetraphenylporphin containing no metal. In the same way, a sublimed film of Mg-phthalocyanine is stable both towards gaseous HCl and towards acetic acid, whereas in acetone solution Mg-phthalocyanine is gradually converted into metal-free pigment when HCl is added [42], and a film of chlorophyll deposited from solution is converted into pheophytin in the presence of acetic acid vapour [43].

Let us turn to the question of the structure of the reaction products formed by phthalocyanine and its stable M--derivatives with acids. Unlike other porphin derivatives, the phthalocyanine molecule has not four but eight nitrogen atoms (VIII), each of which is capable of acting as a proton acceptor. Evstigneev and Krasnovskii observed a marked displacement towards longer wavelengths of the red absorption band of metal-free phthalocyanine and Cu--phthalocyanine when these compounds were dissolved in concentrated H_2SO_4. Since this displacement was not observed in the case of chlorophyll, it was suggested that in acid medium the protons are attached not to the pyrrole nitrogens but to the peripheral N atoms of the phthalocyanine [44]. In a study of ionic equilibrium in solutions of phthalocyanines in H_2SO_4, Berezin [45,46] concluded that the solutions of both the metal-free phthalocyanine and the M-phthalocyanines contain only the cations H_2PcH^+ and $MPcH^+$, where Pc is the ligand in the M-phthalocyanine molecule; he also suggests that the proton is attached to the peripheral N atom. Comment on these conclusions is necessary.

Firstly, it is known that, when Cu-tetraphenylporphin, which is stable in this solution and has no peripheral N atoms, is dissolved in H_2SO_4, the displacement of the absorption towards longer wavelengths, characteristic of the reactions of compounds of the porphin series with acids, is observed [47]. In this case there is apparently no reason to doubt that the protons can be attached only to the pyrrole N atoms, although they are also joined to a metal atom, which creates steric hindrance for this attachment. The possibility of attachment of protons to the pyrrole N atoms in metal-free phthalocyanine is also confirmed by the possibility of H → D isotope exchange in the imino-groups in the presence of DBr.[41]

Secondly, in the reaction with gaseous HCl or HBr the M-phthalocyanine molecule may add one or more protons. Grounds for this statement are provided by the stepwise nature of the desorption of HCl from M-phthalocyanine, revealed in the associated sequence of changes in the infrared spectra of the specimens [41].

It must evidently be assumed that both the pyrrole nitrogen atoms and the peripheral nitrogen atoms of the phthalocyanine molecules may react with protic acids, depending on the conditions.

Important evidence confirming the ionic structure of the products of the reaction of phthalocyanines with gaseous HCl, HBr, and acetic acid is provided by the infrared spectra of these products [41]; absorption bands corresponding to the vibrations of the ionic NH^+ and CH_3COO^- groups can be readily identified. The ionic structure of tetraphenylporphin and tetraphenylchlorin hydrochlorides is confirmed by the presence of absorption bands [34,35] due to the NH^+ groups in their spectra.

The influence of the central metal atom in a phthalocyanine molecule on the ability of this molecule to form hydrochlorides and hydrobromides [41] is remarkable. Thus Mg-, Zn-, and Fe-phthalocyanines react with HCl to form the corresponding hydrochlorides, whereas Cu-phthalocyanine and the metal-free phthalocyanine do not react. All the above phthalocyanines react with the more active HBr molecules. We shall see later that this ability of the central metal atom to facilitate intermolecular interaction between the pigment and the medium is shown not only for HCl and HBr but also for a number of other compounds.

The salts formed by the cations of porphin derivatives are generally readily decomposed with formation of neutral molecules. Thus phthalocyanine hydrochlorides and hydrobromides are converted into neutral phthalocyanines when the specimens are heated in a vacuum to 280–300° or kept in pyridine vapour (an organic base). In concentrated sulphuric acid phthalocyanine cations are converted into neutral molecules when the solutions are diluted with water. Tetraphenylporphin and tetraphenylchlorin are also regenerated from their hydrochlorides with increase in temperature or by treatment with pyridine.

2. Complexes. Let us examine the complexes formed by compounds of the porphin series with the medium, where

the reaction of the components is not so clearly ionic as in the reaction of the pigments with strong acids and bases. Such complexes may be formed in the reaction with comparatively weak bases (aniline, pyridine, or hydrazine), NO, CO, water, and other compounds. The formation of complexes may take place in solutions or when the pigments in the solid state are brought into contact with various gaseous compounds. The process of complex formation is generally reversible.

The ability of metal derivatives of the porphin series to form complexes is much greater than that of the corresponding metal-free pigments. This is apparently due to the ability of certain metal atoms to form additional coordinate bonds as well as valence bonds and to the ability of these atoms to activate the tetrapyrrole ligand with respect to various reactions, including complex formation. The metal atoms in M-derivatives of the porphin series can be divided into three classes [12] according to their coordinating power:

1. Fe, Co, and Mn have a coordination number of 6. In the pigment molecule these atoms are combined with four nitrogen atoms and are able to combine with a further two molecules of a ligand by means of coordinate bonds. The resulting complex has the structure of an octahedron whose centre is occupied by the metal atom and whose apices are occupied by the four nitrogen atoms, joined to the metal atom, and two molecules of a ligand at right angles to the plane of the pigment molecule.

2. Mg, Zn, and Cd have a coordination number of 5 and combine with one additional molecule of a ligand. The complexes have the shape of a four-sided pyramid. The metal atom lies at the centre of the base of the pyramid, the N atoms lie at the corners of the base, and the ligand molecule occupies the fifth apex of the pyramid above the plane of the pigment molecule.

3. Cu and Ni are very weak complex-forming atoms and generally retain the coordination number 4. All free main and coordinate valencies are satisfied by the nitrogen atoms of the tetrapyrrole ring of the pigment molecule. This classification is not rigorous. It is suggested, for example, that in some cases Mg-, Zn-, and even Cu-porphyrins form complexes with an octahedral structure [26,27,48].

As expected, the stability of the complexes decreases with increase in temperature [48,51]. Moreover, it depends to a marked extent on the nature of the central metal atom. Thus direct measurements of the constants for the equilibrium between the monopyridine complexes and free molecules of M-tetraphenylporphin in benzene solution in the presence of small quantities of added pyridine showed that the stability of the monopyridine complexes decreases in the order: Zn, Cd, Hg, and Cu. It is suggested that Mg-tetraphenylporphin and Mg-tetraphenylchlorin, unlike the other metal derivatives studied, form bispyridine complexes under these conditions. On going from porphin to chlorin, there is a slight increase (compared with the change on going from one metal atom to another) in the stability of the pyridine complexes [49].

The formation of complexes by the pigment with a ligand generally leads to changes in the spectroscopic characteristics of both reacting components. These changes are observed not only in the electronic spectra but also in the vibrational spectra [52-55], in the fluorescence spectra [58], and in the photoelectric conductivity [57] of the pigments. The spectroscopic changes on complex formation are more marked, the more stable the resulting complex. They are very marked in the absorption spectra of the Fe-porphyrins, which give particularly stable complexes in their reactions with CO, pyridine, and water [12]. In these cases the appearance of the spectrum of the pigment changes completely. When less stable complexes are formed, the absorption bands are displaced with a more or less marked change in intensity [49,51,52]. Weak interaction between the components in the complex may not produce changes in the electronic spectra of the pigments capable of being recorded at the present stage of development of spectrometric technique. In this case evidence for complex formation is obtained indirectly. For example, in a study of the quenching of the fluorescence of chlorophyll and pheophytin by various oxidising agents and reducing agents it was found that in some cases quenching is observed at concentrations of the quenching agent equal to the concentration of the pigment. Further increase in the concentration of the quenching agent did not lead to an increase in quenching. This phenomenon can apparently be attributed to the formation of complexes between the molecules of the pigment and the quenching agent, although the existence of these complexes is not revealed by the electronic spectra [59].

The electronic absorption spectra of the ligands in complexes with tetrapyrrole pigments have unfortunately not yet been observed, since the pigments and solvents themselves absorb in this range. In the infrared spectra of solid films of M-phthalocyanines it has been possible to observe the absorption bands of indole, aniline, benzylamine, water [52-54], and nitric oxide [55], attached to the pigments from the gaseous phase.

There is apparently no reason to doubt that the central metal atom in molecules of the porphin type is the most probable centre at which a ligand molecule exhibiting electron-donating properties is attached in the formation of a complex. The bond formed between the central metal atom and the ligand molecule is a donor–acceptor bond. This structure for the complex is confirmed by the following evidence: (1) the complexes formed by metal-free pigments with electron-donating molecules are not so stable as those formed by metal derivatives; (2) the frequencies of the absorption bands of aniline, benzylamine, and indole in their complexes with M-phthalocyanines depend to a marked extent on the nature of the metal atom [52,53]; and (3) the magnetic susceptibility of Fe^{II}-phthalocyanine decreases on complex formation with NO, indicating pairing of the *d* electron of the Fe atom with the unshared electrons of the N atom of the nitric oxide [55].

The possibility that the ligand molecules are localised at other active centres in the structure of the pigment molecule cannot, however, be denied. These centres include particularly the pyrrole N atoms, which carry unshared electron pairs and which can therefore take part in the formation of donor–acceptor bonds, including the formation of hydrogen bonds of the type N...H–X. In the spectra of the complexes formed by indole with Mg- and Zn-phthalocyanines, in the range of the stretching vibrations of the NH bonds, it is possible to observe two absorption bands instead of the single band characteristic of free indole (solution or solid layer) [52,53]. These bands apparently correspond to complexes of different type: the comparitively narrow high-frequency band corresponds to indole molecules attached to the metal atom and the broad low-frequency band corresponds to indole molecules joined to

the pyrrole nitrogen atom by a hydrogen bond. An analogous explanation can also be given for the spectra of aniline and benzylamine, which in their complexes with certain M-phthalocyanines give more absorption bands in the range corresponding to the NH bonds than in the spectra for the liquid state[52,53]. The fact that the metal-free phthalocyanine is unable to form complexes with indole, aniline, and benzylamine does not mean that the molecules of these compounds in the complexes with M-phthalocyanine are necessarily attached to the metal atom. As already noted, the inclusion of a metal atom in the phthalocyanine molecule leads to a significant change in its properties, and groups which were previously inactive become active. Thus the metal atom activates the phthalocyanine molecule towards HCl molecules, which are undoubtedly attached not to the metal atom but to the nitrogen atom[42].

In organic solvents in the absence of moisture chlorophyll forms stable 1 : 1 complexes with the metal chlorides $FeCl_3$, $HgCl_2$, $BeCl_2$, $AlCl_3$, $BiCl_3$, $NbCl_5$, and $SnCl_2$, and also with $AgClO_4$. These complexes, whose formation leads to marked spectroscopic changes in the pigment, can be isolated from solutions in the solid form[60-62]. With the passage of time, the chlorophyll in complexes with metal chlorides is gradually converted into the corresponding M-pheophytin. This leads to the suggestion that, when the metal ion of the halide forms a complex with chlorophyll, it establishes a bond with the nitrogen atoms of the pyrrole rings, leading to the possibility of conversion of the chlorophyll into M-pheophytin[60].

Let us consider separately the reaction of phthalocyanines and chlorophyll with water. In air Mg-phthalocyanine forms a stable dihydrate[63]. A dihydrate, slightly less stable than the dihydrate of Mg-phthalocyanine, is also formed by Be-phthalocyanine[64]. The infrared spectrum of an Mg-phthalocyanine specimen kept in water vapour, in the range of the stretching vibrations of hydroxy-groups, shows an absorption band consisting of several components[54]. The characteristic isotopic displacement of this band when H_2O is replaced by D_2O and its disappearance on treatment in a vacuum at 50–100° show unambiguously that this band is due to molecules of water in a complex with Mg-phthalocyanine. Since on treatment of the specimen in a vacuum the components of this band do not disappear simultaneously from the spectrum[54], it may be assumed that the two water molecules in the Mg-phthalocyanine dihydrate are joined to the pigment in different ways. This difference is possibly due to a difference in the localisation of the water molecules in the complex. It is possible to picture a scheme in which one water molecule is coordinated to the magnesium atom via its oxygen atom. The resulting complex has a pyramidal structure in which the magnesium atom has a coordination number of 5. The second water molecule is joined to the nitrogen atoms of the Mg-phthalocyanine molecule by a hydrogen bond on the other side of the pigment molecule.

The stepwise character of the desorption of the water molecules from Mg-phthalocyanine may be given a different explanation, according to which the two water molecules are joined to the central magnesium atom to form a complex with an octahedral structure. As the water is desorbed, the Mg-phthalocyanine dihydrate is converted first into a monohydrate with a pyramidal structure and then into the anhydrous pigment. The states of the water molecules in the Mg-phthalocyanine dihydrate and monohydrate should naturally be different, leading to spectroscopic differences in the infrared range. In this interpretation, however, it is difficult to explain the extremely complex structure of the absorption band of the water joined to Mg-phthalocyanine, so that the first explanation (a difference in the localisation of the two water molecules in Mg-phthalocyanine dihydrate) is to be preferred.

Like Mg-phthalocyanine, chlorophyll adds on water molecules[1]. In this case, however, we cannot speak of the existence of hydrates with definite composition: the decisive feature is the conditions under which the reaction between chlorophyll and water takes place[29]. The infrared absorption spectrum of the water in the complex with chlorophyll depends to a marked extent on the state of the pigment. In the spectra of chloroform solutions and amorphous chlorophyll film the structureless band at 3400 cm^{-1} is similar to the absorption band for liquid water[24]. In the spectrum of a crystalline film of chlorophyll *a* the absorption band for the water, like the absorption band for water joined to Mg-phthalocyanine, consists of several components[31]. This suggests that the localisation of the water molecules is approximately the same in the complexes with chlorophyll and Mg-phthalocyanine. The absence of structure in the absorption band for water joined to chlorophyll in solutions and in the amorphous film can be attributed to the interaction with one another of the water molecules in neighbouring complex molecules. This interaction is reduced to a considerable extent when the complexes are arranged in ordered fashion in the crystalline specimens.

It is suggested that, on contact with chlorophyll, the water molecules may react with the carbonyl group of the cyclopentanone ring[65,66]. This possibility cannot be denied, but the reaction of a water molecule with the keto-group of the cyclopentanone ring is apparently insufficiently strong and does not determine the location of the molecule in the complex with chlorophyll. As in the complex with Mg-phthalocyanine, the water molecules are apparently localised at the N and Mg atoms of the chlorophyll molecule. This suggestion is confirmed by the following evidence: (1) complexes with water are formed not only by chlorophyll, but also by Mg-phthalocyanine, which has no cyclopentanone ring; and (2) although pheophytin and Cu-pheophytin, like chlorophyll, have a cyclopentanone ring, they form only comparatively weak complexes with water[24]. This cannot be attributed to the influence of the central magnesium atom on the cyclopentanone ring, since the similarity in the absorption bands of the keto-groups of chlorophyll, pheophytin, and Cu-pheophytin in the infrared range[24] shows that the influence of the metal atom on the keto-group of the cyclopentanone ring is slight. In the complexes with pheophytin and Cu-pheophytin water molecules are apparently localised at the pyrrole nitrogen atoms.

The structure of the absorption bands for water in complexes with Mg-phthalocyanine[54] and crystalline chlorophyll[31] in the range of its stretching vibrations indicates that strong distortion of the H_2O molecule takes place when it is attached to the pigment. In particular, the presence of broad components extensively displaced towards lower frequencies in the structure of these bands indicates a considerable decrease in the strength of the bonds between the H atoms and O atoms in the water molecules, that is, it indicates a partial positive charge on the H atoms in these molecules. In the green leaf this "dark" partial dissociation of the water molecule possibly precedes the fundamental photochemical step leading to complete splitting of the H_2O molecule followed by the formation of the primary products of photosynthesis.

3. Complexes with charge transfer. In some cases derivatives of the porphin series form complexes, illumination of which leads to transfer of an electron from one of the components of the complex to another. In the process the neutral complex acquires an ionic structure, whose existence, however, cannot be prolonged, since the structure is energetically unstable, and the electron is returned with the liberation of a quantum of energy in the form of heat[67]. A charge-transfer complex is detected spectroscopically by the appearance of a specific absorption band which corresponds to the transition between the energy levels characterising the complex in the neutral ground state and in the excited state with ionic structure.

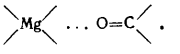
The study of charge-transfer complexes of the porphin series is extremely important, since these complexes may be intermediates in various photochemical reactions of the pigments. Only preliminary work has as yet been carried out in this field, however. It has been found that etioporphyrin, tetraphenylporphin, and Zn-tetraphenylporphin in solution form 1 : 1 complexes with trinitrobenzene. The system absorbs in the region of 500 mμm, which has been attributed to charge transfer in the complex[68]. 1 : 1 charge-transfer complexes are also formed by Zn-phthalocyanine with trinitrobenzene, trinitrotoluene, and other compounds[69]. In all these cases the partners of the porphin derivatives in the complexes are typical electron acceptors, so that in the excited state the pigment molecule forms a positive ion. Since porphin derivatives are amphoteric, we may expect the existence of complexes in which electron transfer takes place from the ligand molecule to the pigment molecule. Electron-donor ligands include triethylamine and ammonia, in the presence of which the spectra of solutions of Mg-etioporphyrin II show a new absorption band, attributed to charge transfer in the complex[70]. The correctness of this interpretation is doubtful, however, since the position of this band in the spectrum (640 mμm) is the same for the complexes formed by the pigment with ammonia and triethylamine, which have quite different ionisation potentials.

4. Association. Association of the molecules of tetrapyrrole pigments with one another is observed in the solid state and in solutions. It is detected in the vibrational and electronic emission and absorption spectra.

In the solid phase phthalocyanines have a crystalline structure; two crystalline modifications, referred to as the α- and β-modifications, are known. The α-modification is less stable and on heating is converted into the β-form. The crystalline structure of phthalocyanine is clearly revealed in the vibrational[20,71,72] and electronic absorption spectra and in the photoconductivity and photoelectromotive force spectra for layers of the pigment[73]. Comparison shows that the infrared spectrum of the β-modification of phthalocyanines is richer than the spectrum of the α-modification with respect to the number of absorption bands and their relative intensity. This is apparently due to the closer packing of the phthalocyanine molecules in the β-form, leading to stronger intermolecular interaction than in the α-form. As a result of the intensification of these interactions, conversion of the α-modification into the β-modification leads to the appearance, in the spectrum of the specimen, of new absorption bands, forbidden for the α-modification. The frequency of the stretching vibrations of the NH groups in the metal-free phthalocyanine decreases in the $\alpha \rightarrow \beta$ conversion, again indicating an increase in the intensity of the intermolecular interactions, in which the imino-groups evidently take part[20]. It is suggested that in the Cu-phthalocyanine crystal (β-modification) the pigment molecule is arranged in such a way that the copper atom interacts with two peripheral nitrogen atoms of neighbouring molecules situated on either side of the plane of the given molecule[74].

Solid chlorophyll, chlorophyllide, and bacteriochlorophyll may exist in either the amorphous or the crystalline state. The spectroscopic characteristics of these states differ appreciably. Thus the red absorption band for chlorophyll *a* lies at 670–675 mμm in the spectrum of the amorphous film and at 692 mμm and 740 mμm in the spectra of the two different crystalline modifications of chlorophyll *a*[75]. Marked differences between amorphous and crystalline specimens of chlorophyll *a* are observed in the infrared absorption spectra[23,24,31]. Unfortunately, the fact that no reliable interpretation has been given for these spectra means that as yet they tell us nothing of the nature of the interaction between the chlorophyll molecules in the solid state.

Association of chlorophyll molecules is observed not only in the solid state but also in solutions. Direct measurements of the molecular weights show that chlorophyll *a* in pure non-polar solvents (CCl_4, benzene, and chloroform) exists in the form of dimers, whereas chlorophyll *b* in benzene forms trimers. In polar solvents, or in non-polar solvents in the presence of small quantities of polar compounds, breakdown of the association complexes takes place and the pigments are present chiefly as monomers. Pheophytin does not form association complexes in either polar or non-polar solvents[26,27]. Association of the pigments leads to changes in their infrared absorption spectra. In particular, there is a decrease in the intensity of the 1700 cm^{-1} band corresponding to the vibrations of the C=O keto-group in position 9 in the cyclopentanone ring, and a new band appears at 1665 cm^{-1}§. This band has been interpreted in different ways. We can apparently reject the interpretation which relates this band to the vibrations of enolised chlorophyll molecules[23-25,30,31], since the proportion of such molecules is small under ordinary conditions (see section II). According to another viewpoint[26-28], the 1665 cm^{-1} band corresponds to the vibrations of the keto-group of the cyclopentanone ring, taking part in the formation of chlorophyll dimers according to a mechanism in which the keto-group is attached by a coordinate bond to the central Mg atom of a neighbouring pigment molecule:

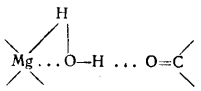


(XVIII)

Vacuum drying of layers of amorphous chlorophyll, however, leads to a decrease in the intensity of the band at 1665 cm^{-1}.[65,66,76] Moreover, the intensity of this band in the spectrum of crystalline chlorophyll (in this case the band is displaced to 1650 cm^{-1}) decreases when the specimen is vacuum-treated and increases again when the specimen is brought into contact with water vapour[31]. These experimental facts are difficult to explain on the basis of the theory that chlorophyll is associated according to mechanism (XVIII). Since the increase in the intensity of the 1665 cm^{-1} band is always accompanied by a decrease in the intensity of the 1700 cm^{-1} band, the suggestion that the 1665 cm^{-1} band is due to keto-groups

§ Katz et al.[26] give for the position of this band in the spectrum the figure 1650 cm^{-1}.

perturbed as a result of intermolecular interactions is convincing. The structure of the chlorophyll association complexes in which this perturbation of the keto-groups takes place is not yet clear, however. In some cases a water molecule is apparently one of the components in the association complexes formed by the chlorophyll molecules. It may be suggested that in crystalline chlorophyll a water molecule attached to the central Mg atom of one of the pigment molecules interacts simultaneously, by means of its partially charged (positively) H atom (see section III, *2*), with the keto-group of a neighbouring pigment molecule according to the mechanism:



(XIX)

In the absence of combined water, association of chlorophyll possibly also takes place according to mechanism (XVIII). The absorption bands of keto-groups associated according to mechanisms (XVIII) and (XIX) have different positions in the spectrum: 1665 cm^{-1} and 1650 cm^{-1} respectively (when crystalline chlorophyll is vacuum-dried, the decrease in the intensity of the 1650 cm^{-1} band is accompanied[31] by its displacement to 1665 cm^{-1}).

The important part played by water molecules in the association of chlorophyll is confirmed by the fact that crystallisation of the pigment takes place only in the presence of water[1]. The ability to form association complexes with the participation of water molecules is characteristic not only of Mg-derivatives of porphin, but also of certain other M-derivatives of this class of compound. It is suggested, for example, that similar association complexes are formed in the presence of moisture in an alcoholic solution of Fe^{III}-pheophorbide[77].

In the presence of polar molecules in chlorophyll solution, the 1665 cm^{-1} absorption band disappears completely and the intensity of the 1700 cm^{-1} band increases. This is attributed to the fact that the polar molecules form coordinate bonds with the Mg atom and lead to disaggregation of the chlorophyll molecules[26]. In addition to changes in the infrared spectrum, the disaggregation of the chlorophyll in solution also leads to significant changes in the electronic spectra: there is an increase in the intensity of the luminescence, which is generally characteristic only of monomeric molecules, and an increase in the intensity of the bands in the absorption spectrum[78,79]. Similar phenomena are observed not only for chlorophyll, but also for a number of other M-derivatives of the porphin series: Mg-phthalocyanine[79], bacterioviridin[80], Ca-, Mg-, and Zn-derivatives of mesoporphyrin, and Zn- and Ca-pheophytins[81].

It was previously mentioned that pheophytin does not associate in either polar or non-polar solvents. Association of the molecules of the pigment can be brought about, however, by adding to its solution a liquid in which the pigment is insoluble. In this way it has been possible to carry out spectroscopic studies of the association of pheophytin, and also chlorophyll, chlorophyllide, and Mg-phthalocyanine in polar solvents[11,82,83]. Gradual increase in the water content of the solution leads to the formation of first dimers and then polymeric aggregates. The red absorption band at 665 mμm for pheophytin in alcoholic solution is displaced to 695 mμm when dimers are formed[82]. The formation of chlorophyll dimers under these conditions leads to a displacement of the red band by only 2 mμm (from 666 mμm to 668 mμm); the formation of chlorophyllide dimers[82] leads to a displacement of 22 mμm (from 630 mμm to 652 mμm). It is suggested[11,82] that, when pheophytin dimerises, the planes of its molecules come into contact. A result of this interaction is the marked bathochromic shift of the pheophytin absorption band on dimerisation. The association of chlorophyll takes place with the direct participation of water molecules, which, by forming coordinate bonds with the Mg atom, do not allow the pigment molecules to approach one another to distances sufficiently short for π-electron interaction. The absence of the phytyl radical from the chlorophyllide molecule makes this interaction possible, despite the presence of combined water.

As expected, increase in temperature leads to disaggregation of the pigments in solutions[82]. Conversely, decrease in the temperature of the solutions to -100° and below leads to dimerisation of chlorophyll molecules even in such polar solvents as alcohol[84,85]. The degree of aggregation of the molecules of tetrapyrrole pigments in solutions also depends on the concentration. This was shown for the trimethyl ester of coproporphyrin by NMR spectroscopy[86].

The type of interaction between molecules of the porphin type in their associates are not limited to the cases examined above. It is evident that in view of the large number of and variety of substituents in the porphin derivatives, they may form association complexes of different structures, depending on the conditions and the properties of the substituents[11].

Thus the problem of the structure of the molecular compounds formed by pigments of the porphin type, and the problem of their role in biochemical processes, are far from being solved. Further spectroscopic studies, including NMR and ESR studies, are necessary. The value of spectroscopic studies will be greatly increased if they are accompanied by kinetic measurements and by chemical analysis of the pigments and the products of their interaction with the environment.

IV. HYDROGEN EXCHANGE IN COMPOUNDS OF THE PORPHIN SERIES

Is it possible for the chlorophyll molecule to exchange its hydrogen atoms with the molecules of the medium, in particular with H_2O molecules? It first became possible to answer this question, which is of fundamental importance for an understanding of the chemical properties and sensitising action of chlorophyll in photosynthesis, when tracer methods were developed. In the molecule of chlorophyll *a* (formula **X**, *a*) all the hydrogen atoms are joined to carbon atoms, which, unlike O, N, and S atoms, do not carry a free pair of electrons in a neutral molecule. In this case hydrogen exchange with water requires a high activation energy. The latter may be decreased in the presence of a catalyst or when the molecule contains electronegative substituents which increase the lability of the hydrogen atoms[87,88] in adjoining CH bonds.

The results of the first work on isotopic exchange between chlorophyll and D_2O or T_2O did not lead to an unambiguous conclusion regarding the possibility of hydrogen exchange between chlorophyll and water[89-95]. Even when isotope exchange was detected, it was not clear whether this involved the H atoms belonging to chlorophyll itself or the H atoms of the water molecules firmly bound to the pigment[94]. The possibility of H → D isotope

exchange between chlorophyll or pheophytin molecules and D_2O molecules was established finally and unambiguously when the products of the interaction of the pigments with D_2O were analysed by infrared spectroscopy[21,43], instead of by measurement of the radioactivity or by the mass-spectrometric method previously employed[89-92]. When films of chlorophyll or pheophytin were brought into contact with D_2O vapour, their absorption spectra showed changes which could be attributed only to H → D exchange involving the hydrogen atoms belonging to the pigment molecules themselves. The nature of the spectroscopic changes taking place during exchange established that the location of the exchanging atoms is the same for the chlorophyll and pheophytin molecules. As expected, pheophytin shows deuterium exchange with the hydrogen atoms of the imino-groups[21]¶ in addition to exchange involving the labile atoms, which are also present in chlorophyll. It was found, moreover, that the nature of the spectroscopic changes in the H → D isotope exchange and hence the location of the exchanging atoms in the pigment molecules are the same for exchange[43] involving CH_3OD, D_2O, or CH_3COOD.

Unfortunately, difficulties in the interpretation of the infrared absorption spectra make it impossible to reach unambiguous conclusions regarding the location of the exchanging atoms in the molecules of chlorophyll and its analogues. The use of NMR spectroscopy has led to considerable progress towards a solution of this problem. Woodward and Škarić[17,96,97] found by NMR spectroscopy that chlorins, unlike porphyrins, are highly sensitive to electrophilic attack in the γ- and δ-positions, that is at the methine bridges adjoining the hydrogenated pyrrole ring of the pigment molecule. This property is revealed, in particular, by the fact that in the presence of CH_3COOD chlorins readily undergo deuterium exchange involving the H atoms in the γ- and δ-positions. Such exchange does not take place in porphyrin molecules. This phenomenon is evidently due to increased electron density in the γ- and δ-positions in the chlorin molecules. Theoretical calculations of the electronic structure in fact show that all the methine bridges of porphin have the same electron density deficit. In the chlorin molecule this deficit is increased in the α- and β-positions but an excess of electron density appears in the γ- and δ-positions[98].

When powerful reagents are used (CF_3COOD, D_2SO_4), isotope exchange in the methine bridges becomes possible even for porphyrin molecules[99], apparently as a result of redistribution of the electron densities in the pigment molecules in the presence of the strong acids.

Woodward's work naturally led to experiments on isotope exchange in chlorophyll and its analogues using NMR spectroscopy. These experiments not only gave independent proof of the possibility of hydrogen exchange in the chlorophyll molecule but also made it possible to solve the problem of the location of the exchanging H atoms. It was shown[32,33,100-102] that, as a result of exchange with deuteriated alcohols, the peaks in the NMR spectra of chlorophyll, pheophytin, and other analogues of chlorophyll, corresponding to the protons in the δ-position and in position 10, disappear, that is, it is in these positions that H → D isotope exchange takes place. The rates of the isotope exchange are different for positions δ and 10. The rate of exchange is also influenced to a marked extent by the presence of the central magnesium atom in the structure of the molecule[33,101]; this is evidently due to a difference in the densities of the electron clouds close to the exchanging H atoms in the molecules of the metal-free and metal-containing pigments.

According to NMR spectroscopy, in the presence of deuteriated alcohols, the H atoms of all three unsubstituted methine bridges in molecules of bacteriochlorophyll (XI) undergo exchange with deuterium[101]. In the presence of deuteriated trifluoroacetic acid, the H atoms of the three methine bridges adjoining the hydrogenated rings in the molecules of octaethylbacteriochlorin with the *cis*-arrangement of the hydrogenated pyrrole rings undergo exchange with deuterium. The rate of exchange of the H atom adjoining two hydrogenated rings is greater than the rate of exchange of the H atoms which adjoin only one hydrogenated pyrrole ring[99].

The rate of isotope exchange in the molecules of chlorophyll and its analogues depends to a marked extent on the acid or basic nature of the medium in which the exchange takes place[21,43,101,102]. More detailed studies of the dependence of the kinetics of exchange on the properties of the pigment and the medium will reveal the mechanism of the isotope exchange, which is not yet clear.

Experiments not directly related to the problems under consideration have been carried out on the biosynthesis of chlorophyll in media containing tracer atoms. It has been possible to prepare completely deuteriated chlorophyll from seaweed grown in almost pure D_2O (99.8%). The absorption spectra of this chlorophyll were recorded in the visible and infrared ranges[103]. Unfortunately, these spectra revealed nothing new for the interpretation of the infrared absorption bands of the pigment. The chlorophyll in chlorella grown in the presence of T_2O shows radioactivity which does not decrease when the chlorophyll is illuminated or treated with alcohols or alkali. The radioactivity decreases, however, when the pigment is oxidised with silver using Fischer's method, in which it is assumed that the hydrogenated pyrrole ring of the chlorophyll molecule is oxidised[104]. If this is the case, it may be concluded that the hydrogenated chlorophyll ring is unable to undergo hydrogen exchange with alcohol, alkali, or water.

V. HYDROGENATION AND DEHYDROGENATION OF THE PYRROLE RINGS IN COMPOUNDS OF THE PORPHIN SERIES

Despite the fact that chlorophyll has recently been synthesised[105-107], the route by which it is formed in the green leaf is not yet clear. It has been proved, for example, that, when etiolated leaves containing protochlorophyll are illuminated, the protochlorophyll is converted almost quantitatively into chlorophyll[1]. Attempts to reproduce this reaction under artificial conditions[108,109], and attempts to carry out the hydrogenation of chlorophyll to bacteriochlorophyll, however, have not yet been successful. In order to investigate the possibility and mechanism of hydrogenation of the pyrrole rings in the molecules of

¶ Isotope exchange in the imino-groups of molecules of the porphin series has been observed repeatedly in studies of the infrared spectra of these compounds[19,21,41]. Since, however, the ability to undergo rapid hydrogen exchange in N–H bonds is a general property of NH-containing molecules, and since there is no reason to distinguish in this connection the tetrapyrrole pigments from other NH-containing compounds, exchange in the imino-groups is not examined here.

chlorophyll and its analogues, it is natural to begin the study with the simplest compound of the porphin series.

1. Dark hydrogenation. The hydrogenation of some porphyrins has been carried out in alcoholic solutions in the presence of sodium [15,16,110-117], in a pyridine + + acetic acid mixture in the presence of zinc [117], in ether or dioxan in the presence of Raney nickel [15], and in pyridine containing hydrazine [118]. Theoretical calculations [119], chemical analysis, and comparison of the spectra of the porphyrin hydrogenation products with the spectra of compounds of known structure have established that these products are the corresponding chlorins, bacteriochlorins, and hexahydro- and octahydro-porphyrins. The reaction of chlorophyll with hydrazine in pyridine solution takes place in two stages. Spectroscopic data indicate that the cyclopentanone ring of the pigment molecule is broken in the first stage and that hydrogenation of the molecule takes place in the slower second stage, leading to the formation of the analogue of bacteriochlorophyll with neighbouring hydrogenated pyrrole rings and a closed cyclopentanone ring [118].

An important feature is that the hydrogenation of the tetrapyrrole pigments was carried out in solutions containing dissolved oxygen. The hydrogenation of tetraphenylporphin, Zn-tetraphenylporphin, and chlorophyll by hydrazine takes place readily in air but not in degassed solutions [118]. The rate of hydrogenation depends on the temperature of the solution and the structure of the pigment molecule. In particular, the reaction rates are different for the metal-free and metal-containing molecules and in the case of the latter they also depend on the nature of the central metal atom [115,117].

2. Photochemical hydrogenation. As in the case of dark hydrogenation, the photochemical hydrogenation of porphyrins in the presence of reducing agents leads to the formation of the corresponding chlorins, bacteriochlorins, and more extensively hydrogenated derivatives [120-123]. The difference lies in the mechanism of the reaction, which takes place readily in degassed solutions under illumination but which in the dark takes place only in the presence of dissolved oxygen (as shown by experiments with tetraphenylporphin, Zn-tetraphenylporphin, and chlorophyll [118]). It may be assumed that the dark hydrogenation is possible only in the presence of molecular complexes formed by the pigment or reducing agent with oxygen, whose formation decreases the activation energy for the introduction of additional H atoms into the pigment molecule. The photochemical hydrogenation evidently involves an optically excited state of the molecule [120], in which the molecule becomes active in the absence of oxygen.

It has already been pointed out that in experiments *in vitro* it has not yet been possible to carry out the hydrogenation of the pyrrole rings of protochlorophyll and chlorophyll without changing the structure of the remainder of the molecule. The assumed formation of the analogue of bacteriochlorophyll with the *cis*-arrangement of the hydrogenated pyrrole rings by the action of hydrazine on chlorophyll [118] is accompanied by irreversible rupture of the cyclopentanone ring of the pigment molecule. It was recently found that, when a concentrated degassed alcoholic solution of chlorophyll containing phenylhydrazine is illuminated, the main absorption bands of the pigment are displaced towards shorter wavelengths [124]; this is analogous to the displacement observed on going from chlorin to bacteriochlorin with the *cis*-arrangement of the hydrogenated pyrrole rings [15,119]. The spectrum of the original chlorophyll is regenerated when the solution is brought into contact with air [124]. It may be assumed that this reaction leads to the formation of the *cis*-isomer of bacteriochlorophyll with a closed cyclopentanone ring, which is insufficiently stable and is oxidised to the original chlorophyll on contact with atmospheric oxygen.

If the properties of the medium are close to those characteristic of green plants, it is possible to select conditions under which protochlorophyll undergoes photochemical reduction to chlorophyll [109]. It is believed that appropriate selection of the medium will make it possible to carry out the further hydrogenation of chlorophyll to bacteriochlorophyll with the *trans*-arrangement of the hydrogenated pyrrole rings, which is characteristic of this pigment. This hydrogenation apparently takes place when the water-soluble "667 protein chlorophyll" is illuminated, leading to a decrease in the intensity of the absorption bands of the original pigment and the production of new bands [125] at 362, 567, and 743 mμm, closely resembling the bands due to natural bacteriochlorophyll.

As in the case of dark hydrogenation, the ability to undergo photochemical hydrogenation depends to a marked extent on the structure of the pigment molecule. For example, illumination of Zn-tetraphenylporphin in the presence of reducing agents leads to its ready conversion into dihydro- and tetrahydro-derivatives [118,120], whereas photochemical hydrogenation of metal-free tetraphenylporphin and tetraphenylchlorin does not take place under the same conditions [34,35].

3. Dehydrogenation of chlorins and bacteriochlorins. The hydrogenation of the pyrrole rings of tetrapyrrole pigments is reversible: the action of oxidising agents under suitable conditions may lead to the conversion of bacteriochlorins into chlorins and of chlorins into porphins. This change can be carried out in the dark or photochemically. For example, unsubstituted chlorin is dehydrogenated to porphin when its solutions are heated in the presence of various quinones [126]. Metal derivatives of chlorin and bacteriochlorin are dehydrogenated much more rapidly than the metal-free pigments [16,126]. Dehydrogenation of bacteriochlorins takes place more readily than the dehydrogenation of chlorins. For example, the *cis*-isomer of octaethylbacteriochlorin is converted immediately into octaethylchlorin by treatment with mineral acids [16], and tetraphenylbacteriochlorin is oxidised to tetraphenylchlorin even by passage through a chromatographic column of talc.[15]

The photochemical dehydrogenation of chlorins by quinones apparently takes place when the pigment molecules are in an optically excited triplet state [119,121,127-129].

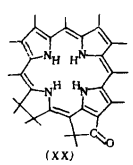
VI. REVERSIBLE PHOTOCHEMICAL REDUCTION OF COMPOUNDS OF THE PORPHIN SERIES

From the time of Krasnovskii's discovery (1948) of the reversible photochemical reduction of chlorophyll [8,130], this reaction has been extensively studied. In particular, it has been established that this reaction is characteristic not only of chlorophyll, but also of many other compounds of the porphin series, and that the final result of the photoreduction is the attachment to the pigment molecule of two or more H atoms which can be readily removed in the presence of an oxidising agent, or even without oxidising

agents, with the regeneration of the original pigment molecule. Up to the present, however, no agreement has been reached regarding the molecular structure of the products of the photoreduction of chlorophyll and other tetrapyrrole pigments. Without going into questions of the mechanism of photoreduction (the formation of primary and secondary photoreduced forms, the influence of the properties of the medium, the part played by complex formation in photoreduction, the influence of the structure, particularly of the central metal atom, on the ability of the pigment molecule to undergo photoreduction, and other topics), we shall concentrate attention in this section on the molecular structure of the photoreduced forms of compounds of the porphin series.

For the red photoreduced form of chlorophyll, Rackow and König proposed a structure in which, as a result of the photoreaction, one H atom is attached to one of the central N atoms and the second is attached to the cyclopentanone ring of the pigment molecule so that the C=O keto-group of the cyclopentanone ring is converted into a C–O–H carbinol group [131]. Serious objections to this structure can be put forward, however. Firstly, the ability to undergo photoreduction is shown not only by chlorophyll but also by a whole series of other tetrapyrrole pigments which do not contain a cyclopentanone ring. Secondly, the infrared absorption band corresponding to the stretching vibrations of the C=O group of the cyclopentanone ring in pheophytin does not disappear from the spectrum after photoreduction of the pigment [132], as would have been expected if the keto-group had been converted into a carbinol group.

Sidorov and Terenin [132] were able to isolate the photoreduced form of pheophytin from solution and to measure its infrared absorption spectrum. On the basis of the spectroscopic data obtained, they proposed the following structure (XX) for the photoreduced form of pheophytin:

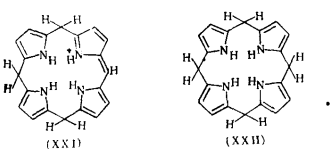


(XX)

Objections to this structure were also put foward, since it was shown that in the photoreduction of mesoporphyrin and tetraphenylporphin the degree of luminescence polarisation of the pigment increases, and this usually corresponds to a decrease in the symmetry of the structure of the luminescent molecules [133,134]. The molecule with structure (XX), however, has a higher symmetry than that of the original pheophytin molecule. Infrared spectroscopy cannot yet give us sufficient information to resolve unambiguously the problem of the structure of the photoreduced porphins. There is also insufficient foundation, however, for the objections to structure (XX) on the basis of polarisation measurements. The molecules of the reduced pigments show an increased tendency to form complexes with the molecules of the medium, leading to appreciable perturbation of the electronic structures of the interacting molecules [122]. These perturbations can undoubtedly lead to breakdown of the symmetry of the molecules and hence to an increase in the degree of luminescence polarisation. From this follows that a high degree of luminescence polarisation, indicating low symmetry of the electronic structures, does not provide sufficient grounds for excluding the possibility of high symmetry for the atomic configurations of the molecules of the photoreduced forms.

On the basis of recent data, it may be suggested that on photoreduction different compounds of the porphin series give products with different molecular structures or, in other words, that the location of the H atoms attached as a result of the photochemical reaction is different for different tetrapyrrole pigment molecules [35,123,135]. The following main classes of porphin molecule can be distinguished, depending on the structure of the photoreduced forms: porphyrins, chlorins, metal derivatives of the porphin series, and phthalocyanines. The number of these classes apparently does not limit the number of possible structures for the photoreduced forms.

Most workers at present ascribe to the molecules of the photoreduced forms of porphyrins a structure of the phlorin type (XIII) [34,97,123,136,137]. The photoreduction of porphyrins often does not stop at the attachment of only two H atoms but proceeds further, leading to the formation of tetrahydro- and hexahydro-porphyrins. According to Mauzerall [136], the latter have the structures of porphomethene (XXI) and porphyrinogen (XXII) respectively:



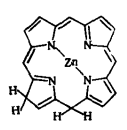
(XXI) (XXII)

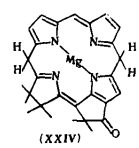
In a study of the properties of various compounds of the porphin series, Gurinovich concluded that the introduction of substituents in the pyrrole rings (positions 1–8) in porphin makes the photoreduction of the pigments more difficult. Tetrabenzoporphin and phthalocyanine do not undergo photoreduction under conditions in which other porphin derivatives are fairly readily reduced [133,138]. This fact, the polarisation studies discussed above [133,134], and certain general chemical considerations led to the suggestion that in the photoreduction the H atoms are attached not to methine bridges, where substitution does not reduce the reactivity of the pigment with respect to photoreduction, but to the pyrrole rings. In the process the two H atoms are attached not to a single pyrrole ring, as in the case of the hydrogenation of porphin to chlorin, but to two rings, with a corresponding redistribution of the double bonds in the molecule [133,134,138,139]. Without denying that hydrogenation of the pyrrole rings is possible in principle in the photoreduction of compounds of the porphin series, one must point out some unsatisfactory features of the arguments put forward in support of this photoreduction mechanism. It is natural that pigments with different structures should have different reactivities with respect to photoreduction under identical conditions. The fact that tetrabenzoporphin and phthalocyanine do not undergo photoreduction under the usual conditions for this reaction does not mean that these pigments cannot be reduced under any conditions. For example, Mg-phthalocyanine gives a photoreduced form under certain conditions [8]. It is then difficult to imagine that the reduction takes place at the pyrrole rings, which in the phthalocyanines are fused with benzene rings.

The infrared absorption spectra indicate that the structures of the photoreduced forms of tetraphenylporphin and tetraphenylchlorin differ significantly [34,35]. The photoreduction of tetraphenylporphin leads to the appearance of

an absorption band in its spectrum at about 2600 cm^{-1}, which can be assigned to the stretching vibrations of the newly-formed C–H bonds. This absorption band is not observed in the photoreduction of tetraphenylchlorin. The infrared spectrum of the photoreduced form of tetraphenylchlorin resembles in many respects the spectrum of its hydrochloride. This leads to the idea that, like the protons in the formation of the hydrochloride, in the photoreduction of the tetraphenylchlorin molecule the H atoms are attached to its two central N atoms. In other words, the molecule of the photoreduced form of tetraphenylchlorin has a structure analogous to that proposed for the photoreduced form of pheophytin (XX). The most probable structure of the photoreduced form of tetraphenylporphin is the phlorin structure. Whether this difference is general for all porphyrins and chlorins is an open question. It is believed that differences should exist in the structures of the photoreduced forms of metal-free pigments and their complexes with metals.

Seely and Talmadge [123] consider it improbable that in the photoreduction of M-derivatives of the porphin series the H atom is attached to a central nitrogen atom joined to the M atom. For the photoreduced form of Zn-porphin, they proposed the structure (XXIII), assuming this to be one of the intermediate forms in the conversion of Zn-porphin into Zn-chlorin. There are as yet no direct experimental facts confirming or refuting structure (XXIII) proposed for the photoreduced form of Zn-porphin. It may, however, be held that this form is not necessarily an intermediate in the conversion to Zn-chlorin. This is indicated by the absence of an intermediate photoreduced form in the photohydrogenation of Zn-tetraphenylporphin to Zn-tetraphenylchlorin in the presence of benzoin or hydrogen sulphide [120-122], although it is known that under illumination in the presence of hydrazine Zn-tetraphenylporphin gives a photoreduced form [122] similar to the photoreduced form of Zn-porphin. It must apparently be assumed that the photohydrogenation of porphins to chlorins may take place without the formation of an intermediate reduced form similar to the photoreduced form of Zn-porphin and Zn-tetraphenylporphin. The photoreduced forms of M-derivatives of porphin, which show an increased reactivity, may undergo various changes depending on the conditions. Chlorins are only one of the most stable final products of these changes.


(XXIII)


(XXIV)

After comparing the spectra of the photoreduced form of ethyl chlorophyllide *a* with the spectra of biliverdin and mesobiliviolin, Seely and Folkmanis [135] concluded that the molecule of photoreduced ethylchlorophyllide does not contain a ring of conjugated bonds covering more than two pyrrole rings. On this basis the photoreduced form of ethyl chlorophyllide was assigned the structure (XXIV) with two hydrogenated methine bridges in the β- and δ-positions. According to the suggestion of Seely and Folkmanis, the photoreduced form of pheophorbide (metal-free chlorophyllide) has two spectroscopically different tautomeric structures: the phlorin structure and a structure similar to structure (XXIV).

To summarise this section, it may be concluded that there are as yet insufficient experimental data for a final solution of the problem of the structure of the photoreduced forms and that all proposed molecular structure schemes are to some extent hypothetical. Further progress in the determination of these structures requires the continuation of systematic spectroscopic studies of the photoreduction of compounds of the porphin series, accompanied by kinetic measurements and chemical analyses.

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CONDITIONS FOR THE FORMATION AND STABILISATION OF THE CARBON–TRANSITION METAL σ BOND

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I. INTRODUCTION

The organic chemistry of the transition metals is a new, rapidly developing branch of chemistry, which already forms the subject of hundreds of investigations, and a large number of complexes of different types have been prepared. Following the discovery of ferrocene and other metallocenes there was the discovery of the analogously constructed sandwich bisarene complexes, cyclopentadienylcarbonyl and arenecarbonyl complexes were obtained, and from about 1957 the area was considerably extended owing to the use of a wide range of alkenes, both cyclic and acyclic. The existences of complexes containing alkenes from ethylene to tropylene suggests that from two to seven carbon atoms from a single molecule can be bonded simultaneously with a metal atom. The best combinations of ligands in such complexes, which make them the most stable, are the combinations of alkenes with CO groups, phosphines, amines, sulphides, acetylacetone, or simple electronegative atoms, such as halogen. Recently, purely alkene complexes have also been obtained and shown to be considerably less stable than the mixed complexes. It was found that all transition metals — without exception — are able to form π-complexes with alkenes. Usually the Dewar–Chatt scheme [1,2] is employed to explain the structure of these compounds. Several reviews and monographs devoted to this field have appeared, among which can be recommended the reviews of Wilkinson and Cotton [3] and Dyatkina [4] on the cyclopentadienyl and arene complexes, Nesmeyanov and Perevalova [5] and Rausch [6] on ferrocene chemistry, Bennett [7], Guy and Shaw [8], the monograph of Fischer and Werner [9] on alkene and alkyne π complexes of the transition metals, the review of Treichel and Stone [10] on fluoroalkyl derivatives of metals. The review article of Fritz [12] is devoted to spectroscopic results, and the theoretical side of the problem has been stated in the books by Orgel [13] and Ballhausen [14], both of which have been published in Russian.

Simultaneously with the study of the conditions for the formation of π complexes many of the conditions for the formation and stabilisation of covalent σ-bonded derivatives of the transition metals were found and although the problem of the carbon–transition metal bond has not been solved completely, the empirical data which have been accumulated allow some conclusions to be drawn. Besides the preparation of many mixed complexes which include a σ-bound organic group, the conditions for the σ derivative →

→ π complex transition and the reverse are now known. A repeat study of some structures showed that in several instances where the π complex structure has been proposed earlier, actually there is the addition of metal to a system of double bonds of the Diels–Alder type and the bonding with the organic molecule is effected by one π and two σ bonds. A large group of fluorocarbon σ complexes of various types has been obtained. Besides comparatively old reviews, a book [15], and Cotton's review [16], the material on the σ-bonded derivatives of the transition metals has not been surveyed. The review we offer is an attempt at such a survey and embraces the literature up to December 1964. The tables do not exhaust the available information, but only illustrate it.

II. THEORETICAL PREMISES

The problem of the transition metal–carbon covalent bond remained an enigma for a long time. As is well known, the hydrocarbon σ derivatives of most transition metals are almost impossible to isolate in a pure state; they are unstable, exist only at low temperatures, are sensitive to oxygen and atmospheric moisture. The latter is inherent, however, in an alkyl derivative of certain non-transition metals, for example, the alkali metals, but is not characteristic of derivatives of Hg, Sn, Pb, etc. Furthermore, the alkyl derivatives of the main groups have a considerably better thermal stability than their transition metal analogues.

The strength of a covalent bond depends on the extent of the overlap of the valence orbitals of both atoms. The instability of the covalent derivatives of the transition metals is connected with insufficient overlap of the completed 3*d*, and also the 4*s* and 4*p* orbitals of the metal in the first transition series with the typical σ orbitals of the ligands, owing to the small dimensions of these orbitals of the metal. Confirmation of the correctness of this conclusion is provided by the fact of the formation of alkyl derivatives of metals with *d* orbitals of the largest dimensions. However, it was acknowledged that the difference in the size of the overlap integrals is not very great and possibly the difficulty of obtaining these compounds is explained, not by their thermodynamic instability, but by their high reactivity. If that is so, when the covalent bond is formed as a donor–acceptor bond, the great strength of the bond facilitates a greater polarisability of the donor molecule and the great affinity of the acceptor ion for an electron. With increase in the charge on the metal ion, its electronegativity, within the limits of a single period of the Periodic System, and also the polarisability of the ligand, the covalency of such ordinary bonds should increase [13].

The transition metal–carbon bond can be either a simple ordinary bond or a bond of multiple character. Carbonyls, cyanides, etc. are examples of comparatively stable and long-known carbon derivatives of the transition metals. The order of the metal–carbon bond in the compounds of these classes is greater than unity, thanks to additional overlap of symmetry-suitable filled orbitals of the metal and free orbitals of the ligand. Fig. 1 shows the different ways of representing the increase in the multiplicity of the metal–carbon bond in carbonyls.

The additional overlap is termed a π bond or dative component of the bond. Usually π bonding, and consequently the formation of bonds of significant multiplicity is an

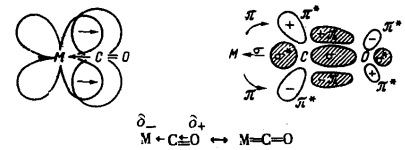


Fig. 1. Different methods of representing the increased multiplicity of the metal–carbon bond in metal carbonyls.

ability of an electronegative atom in the vicinity of carbon, such as oxygen in carbonyls, nitrogen in cyanides, etc. In explaining the properties of the derivatives of transition metals, the π component of the bond plays an important part. The excess of negative charge is removed from the metal with its aid to the ligand and double-bond character appears, which in total leads to the strengthening of the bond and increases the stability of the molecule as a whole. Actually, without such an assumption of reverse transfer of electrons from the metal to the ligand it would be difficult to understand why in the majority of their most stable derivatives transition metals have an electron configuration of a noble gas, that is, they receive from 8 to 15 electrons, which generally is not characteristic of metals. The reverse transfer does not occur with simple alkyl derivatives, since they do not have low-lying free orbitals. Furthermore, the establishment of a cyclic configuration due to σ groups alone is evidently impossible from even steric considerations.

All this does not explain, however, why the alkyl derivatives of transition metals should be less stable than the alkyl analogues with non-transition metals and why just carbon is so poorly bonded with the transition metal. As will be shown below with the help of experimental data, the transition metals can under certain conditions form stable σ bonds with carbon. In such molecules, in addition to the σ bound group stabilising ligands are present — carbonyl, phosphine, cyanide, or cyclopentadienyl groups. These mixed complexes are often very stable and represent a contrast to the extremely unstable simple organic derivatives of the MR_n type.

Chatt and Shaw [17,18] consider that the peculiarity of the transition metals is that the *d* orbitals of the penultimate layer are energetically close to their *s* and *p* valence orbitals. This creates the possibility of easy transition of non-bonding electrons from the higher occupied *d* orbital to the antibonding orbital of the metal–carbon bond. When the *d* orbital is vacant then the reverse transition from the orbital of the metal–carbon bond to this vacant orbital is possible. One or the other should weaken the M–C bond, the transfer of electrons is the first stage in the rupture of this bond. Fig. 2 shows the scheme of the energy levels of the vacant and occupied orbitals of the metal atom. To form a stable complex the energy difference of the highest occupied and the lowest vacant orbital ΔE should be greater than some critical value. Chatt and coworkers made several alkyl and aryl derivatives of the metals of Group VIII, stabilised by tertiary organic phosphines. The authors connect the stabilising role of the ligands with the fact that their addition to the metal allows ΔE to be increased. This is brought about by the formation of a strong dative bond with the metal as the result of the involvement of the non-bonding electrons of the highest occupied level in the formation of a bond with this ligand

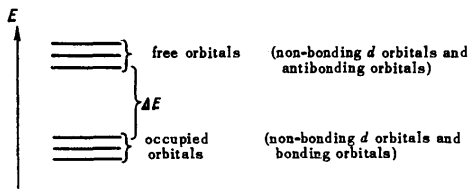


Fig. 2. Suggested condition of stability of covalent organic derivatives of the transition metals.

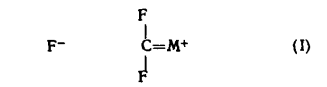
which leads to the lowering of the level, that is, to an increase in ΔE. In square-planar and octahedral complexes the stabilising influence of such ligands is greater than in tetrahedral. With the heaver transition metals the splitting of the orbitals is greater than in the lighter ones and there is a greater capability to form dative bonds. Therefore the heavy metals should give more stable organic σ derivatives, which is what occurs in reality. This is the reverse of what is observed for all the other elements of the Periodic System, where the heaviest element in each subgroup forms the least stable organic derivatives. The zinc group is an exception, where there is no true relationship: the mercury derivatives are thermally more stable, but the chemical reactivity is completely the reverse. Chatt considers that in the zinc group there is still a shade of transition metal character.

The cleavage of the metal–carbon bond is irreversible and it is evident, therefore, that as a result a very active particle is produced — a radical or carbanion. Unlike this, the metal–halogen bond, for example, can be broken reversibly since the halide anion is stable and can exist until it is possible for the broken bond to be reformed.

Behaviour towards oxygen and moisture, that is, towards chemical reaction, also enters into the concept of stability — which is generally not very definite. Apparently, complexes which have available free or only partly occupied orbitals will be sensitive to nucleophilic attacks.

Jaffé and Doak [19] calculated the bond energy in alkyl and aryl derivatives of transition metals and drew the following conclusions about the reasons for the instability of these compounds: (1) the bonds with transition metals have only one-third of the energy of ionic resonance which makes stable the alkyl derivatives of the alkali metals, (2) they have only one-half of the covalent energy which makes stable bonds with all the other elements. The aryl σ derivatives are somewhat more stable than the σ alkyl derivatives. This is due to the increase in the s character of the bonds formed by the sp^2 orbitals in comparison with the sp^3 orbitals, which is favourably reflected in the ionisation potential, the overlap integral, and the ionic resonance energy of the M–C bond, and also the large electronegativity of the sp^2 orbitals of carbon compared with the sp^3 orbitals. The same conclusions are drawn in respect of the vinyl and ethynyl derivatives and are also confirmed experimentally.

Starting from Jaffé and Doak's conclusions that the instability of the simple transition metal–carbon bond can be linked with the low ionic resonance energy, a group of investigators [20,21] concluded that σ-bound fluorocarbon derivatives of the transition metals should exist. The effective electronegativity of the CF_3 group is ~ 3.3 on the Pauling scale and is situated between those for fluorine (4.10) and chlorine (3.0) [22]. The effective electronegativity of the C_6F_5 group is approximately equal to that for bromine (2.8). Therefore the ionic character of the metal–carbon bond should increase on going from hydrocarbon to fluorohydrocarbon derivatives. And although fluoroalkyls — like alkyls — cannot participate in π bonding, the metal–fluoroalkyl bond should be considerably more stable. The bonding electrons of such bonds are drawn out towards the fluorocarbon group, decreasing the charge on the metal. The spectroscopic data for them confirm the essential importance of structure (I):



(I)

The preparation of a large number of fluorocarbon derivatives of different type, the ease with which they are obtained, and the stability (both thermal and chemical) of most of them confirms the general correctness of the premises.

Hence the stability of a complex depends on various factors, the influence of which is not always understood and cannot *a priori* be predicted and explained. We will turn therefore to the experimental data, classified according to the groups of the Periodic System. Fluorinated σ complexes will be considered in parallel.

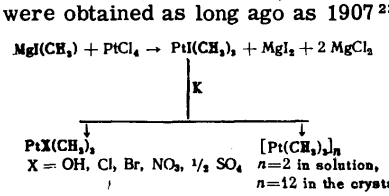
As a review on a similar theme by Razuvaev and Latyaeva was recently published [11], which described in detail the chemistry of organotitanium compounds†, we exclude Group IV from consideration. The copper subgroup is also not considered here, as there is already a sufficiently complete review [15].

III. EXPERIMENTAL DATA

1. Group VIII

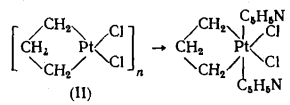
Platinum, palladium, nickel. In addition to the comparatively stable alkyl derivatives of platinum of composition $PtXR_3$, PtR_4, $[PtX_2R_2]_n$, the following types of mixed complexes have been obtained for this group of metals: $PtX_2R_2L_2$, $MXRL_2$, MR_2L_2, MXR_fL_2, and $MR_f{}_2L_2$, where M = Pt, Pd, Ni; L is a unidentate ligand of the organic phosphine type; X halogen; R alkyl or aryl; R_f a fluorocarbon radical; Ni-(π-C_5H_5)R(PR_3), Ni-(π-C_5H_5)R_f(CO), $K_2M(C{\equiv}CR)_4$, and $K_2M(C{\equiv}CR)_2$ for all three metals. A systematic comparison of the stability was made for the example of square-planar phosphine complexes MR_2L_2, and it was shown that their stability varies in the order: $NiR_2L_2 < PdR_2L_2 < PtR_2L_2$.

The platinum(IV) alkyl derivatives are the most stable of the known transition metal alkyl derivatives. The first of these, iodotri(methyl)platinum(IV), and some of its derivatives were obtained as long ago as 1907 [23,24].



† The review mentioned [11] covers the covalent organometallic compounds of the transition metals of Groups IV–VIII (Ed. of Translation).

Subsequently, in the repetition of this work[25-27], in addition to iodotri(methyl)platinum(IV) and tetramethylplatinum(IV), diiododi(methyl)platinum(IV), triiodo(methyl)-platinum, etc. were isolated. There are also other paths for obtaining iodotri(methyl)platinum(IV), for example, the alkylation of tetrachloro-dipyridino-*cis*-platinum(IV) with a Grignard reagent[28] or the reaction of methylmagnesium iodide with Zeise's salt‡ or with Na_2PtCl_4 in the presence of an excess of methyl iodide[2,29]. Gilman and coworkers found[25,26] that tetramethylplatinum(IV), isolated originally as a side-product, can be obtained satisfactorily from iodotri(methyl)platinum(IV) and methylsodium. It is crystalline and without a definite melting point or decomposition temperature. Tetramethylplatinum, etc. are of special interest because of their tetrametric structure[30], which is shown in Fig. 3. The bridge function of the methyl groups is unusual, although also not unprecedented. Halogen, sulphur, or phosphorus atoms, which have free electron pairs, are most often encountered in such a role. The formation of the tetramer, and also the solvation and association in solutions reflect the coordination unsaturation of the platinum atoms and the tendency to add on more than four groups. In these compounds, and also in alkylacetylacetonatomethylplatino and similar dimers[31-34] platinum tends to become 6-coordinate. Unlike these complexes, cyclopentadienyltri(methyl)platinum(IV) is monomeric[35]. Chatt and coworkers isolated the polymeric trimethyleneplatinum complex(II) from the reaction between H_2PtCl_6 and cyclopropane[36]. The polymerisation is effected by means of halogen bridges, as was confirmed by the breaking down of the polymer with amines. Phosphines replace the trimethylene ligand, both in the polymeric complex and in the pyridine-containing monomer.

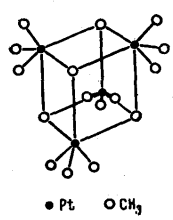


(II)

Platinum(IV) derivatives are also obtained by addition of alkyl halide to certain platinum(II) complexes or by oxidation of the latter with halogens[17]:

$$PtI(CH_3)(PR_3)_2 + CH_3I \rightarrow PtI_2(CH_3)_2(PR_3)_2,$$
$$Pt(CH_3)_2(PR_3)_2 + Cl_2 \rightarrow PtCl_2(CH_3)_2(PR_3)_2.$$

σ-arylphosphine complexes are obtained similarly. Derivatives of the $PtAr_4$ type have not been obtained pure, although there are indications that a mixture of phenyl derivatives is formed in the reaction of $PtCl_4$ with bromo(phenyl)magnesium[27].



• Pt ○ CH_3

Fig. 3. Structure of tetramethylplatinum, after Rundle[30].

‡ $K[PtCl_3(C_2H_4)]$ (Ed. of Translation).

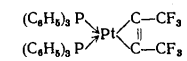
The simplest platinum(II) derivatives PtR_2 are unknown, but platinum(II) complexes are easily alkylated, giving stable crystalline square-planar complexes, which exist as *cis*- and *trans*-isomers[17,37]:

$$PtX_2(PR_3)_2 + 2MgXR' \text{ or } 2LiR' \rightarrow PtXR'(PR_3)_2 \text{ or } PtR'_2(PR_3)_2.$$

The alkyl groups of such complexes are detached by the action of acids or salts like magnesium iodide[17]. Analogous aryl and ethynyl complexes are obtained which are usually more stable than the alkyl complexes.

Halogeno(alkyl)phosphine complexes of platinum and palladium are known to undergo the reaction termed carbonylation, in which CO from the gas phase is inserted at the R–M bond[38]. This interesting reaction, characteristic of many complexes, will be considered in detail below. In the present example, typical acyl derivatives capable of the reverse, decarbonylation, with recovering of the initial substance, are obtained.

As is well known, the reaction of platinum derivatives with alkynes leads to the formation of π complexes of the Zeise's salt type, where acetylene is present instead of ethylene. Such a structure is confirmed by the infrared spectra, in which there are frequencies of coordinated triple bonds, and also the regeneration of acetylene as a result of various effects. Perfluorobut-2-yne is an exception, and is reported[39] to add on by two σ bonds, giving (III):



(III)

Yet another type of alkyne derivative of platinum, palladium, and nickel is obtained — acetylido-complexes, for example, $K_2Pt(C{\equiv}CR)_4$, which are non-explosive, diamagnetic complexes, which on reduction give pyrophoric $K_2Pt(C{\equiv}CR)_2$, readily oxidised to tetraalkynylplatinates[40].

The simplest organic derivatives of palladium and nickel have not been described although attempts to obtain them have been made[16] and there is indirect confirmation of their existence. Just as for platinum, square-planar mixed complexes of composition MR_2L_2 or $MXRL_2$ are characteristic for palladium, where R can be alkyl, aryl, or ethynyl[41]. For nickel, only aryl and ethynyl derivatives have been obtained[42,43]. Only the *trans* forms of these Pd and Ni complexes have been isolated. Aryl derivatives of nickel exhibit moderate stability with the exception of those whose aryl groups have *ortho*-substituents. For example, $[NiBr\{2,4,6\text{-}(CH_3)_3C_6H_5\}\{P(C_2H_5)_3\}_2]$ sublimes in the atmosphere at ~ 160° at normal pressure.

The general theory of stability and the stabilising effect of some ligands were considered above. Fig. 4 shows the splitting of the levels of the *d* orbitals in planar complexes of type d^8 analogous to the organometallic derivatives being considered[44]. The stability of these complexes thus depends on the difference in the energy of the least stable $d_{x^2-y^2}$ orbital and d_{xy} orbital lying in the plane of the molecule. Evidently in alkyl phosphine derivatives of nickel, the splitting of the *d* levels is insufficient to stabilise them and the necessary value is reached only in aryl complexes. Unsubstituted phenyl groups are capable of free rotation around the metal–carbon bond; in this, their π orbitals overlap with the d_{xy}, d_{xz}, and d_{yz} orbitals, somewhat lowering all these levels and increasing ΔE the more so. In this way the metal–phenyl bond acquires some degree of multiplicity, making worse the mesomeric electron displacement from the metal to the phenyl group.

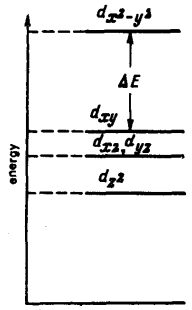


Fig. 4. Scheme of energy levels of the *d* orbitals for square planar configuration.

This makes them more stable in comparison with the alkyl derivatives. With *ortho*-substituted aryl derivatives, bulky substituents prevent free rotation, the aryl group is held in the plane perpendicular to the plane of the complex. In that position the π orbital of the aryl group should react preferentially with the d_{xy} orbital, hence ΔE will be greater than when there is free rotation. The increase ΔE prevents the thermal dissociation of the complex, leading to breaking away of the free radical and the screening of the metal atom by the ortho-substituents hinders the attack by chemical reagents. *Meta*- and *para*-substituted aryl complexes are analogous to the unsubstituted phenyl and — depending on the substituent — somewhat increase or decrease ΔE.

All these complexes are obtained from metal halogeno--complexes and Grignard reagents or alkyllithiums, some of which are shown in Table 1.

A recent paper by Yamazaki and Hagihara[45] describes the production of the first σ alkyl complexes of nickel which contain π-cyclopentadienyl and phosphine groups in the molecule:

$$NiCl(\pi\text{-}C_5H_5)P(C_6H_5)_3 + MgIR \rightarrow NiR(\pi\text{-}C_5H_5)P(C_6H_5)_3,$$

where R = CH_3, C_2H_5, C_6H_5, C≡CH, etc. The least stable of these are again those with alkyl groups. They are all comparatively difficult to decompose by heating, but the solutions are unstable, especially in air. It is interesting to note that attempts to obtain $NiR(C_5H_5)(CO)$ did not give a positive result, although the formation of a labile non--isolable methyl derivative was proved spectroscopically.

Hence the combination of π-cyclopentadienyl and phosphine is so effective that it allows stable alkyl derivatives of nickel to be obtained.

The high electronegativity of R_f groups is due to the pseudo-halogen nature of the perfluoroalkyl iodides. In

TABLE 1. σ derivatives of platinum, palladium, and nickel.

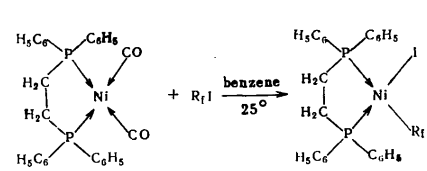
Derivative*	Colour	M.p., °C	Reference			
			preparation	infrared spectra	NMR	dipole moment
$(CH_3)_4$ Pt	white	—	26	—	—	—
$(CH_3)_3$ PtI	orange-yellow	195—200 (decomp.)	26	—	—	—
$(CH_3)_2$ PtI_2	black	—	26	—	—	—
CH_3PtI_3	»	—	26	—	—	—
$(CH_3)_3$ PtI (pyridine)$_2$	white	168	28,31	—	—	—
$[(CH_3)_3$ Pt(acetylacetone)$]_2$	»	200 (decomp.)	31,32	—	—	—
$[(CH_3)_3$ Pt $(CH_3CH_2CO)_2$ $CH_2]_2$	»	190 (decomp.)	32	—	—	—
$[(CH_3)_3Pt]_2$	pale yellow	explodes	26	—	—	—
$[(CH_3)_3$= $PtCl_2]_n$	yellow	148 (decomp.)	36	36	36	—
$(CH_3)_2$ = $PtCl_2$(pyridine)$_2$	white	140—145	36	36	36	—
$(CH_3)_2$ PtC_6H_4	»	65	35	—	35	—
$(CH_3)_2$ Pt $(Cl)_2$ [P $(C_2H_5)_3]_2$	»	114—117	17	—	—	17
$(C_6H_5)_2$ $(Cl)_2$ Pt [P $(C_2H_5)_3]_2$	»	153—155	17	—	—	17
cis-$(CH_3)_2$ Pt [P $(C_2H_5)_3]_2$	»	81—82	17	37	—	17
trans-$(CH_3)_2$ Pt [P $(C_2H_5)_3]_2$	»	76—79	17	—	—	17
trans-$(C_6H_5)_2$ Pt [P $(C_2H_5)_3]_2$	»	176—180	17	—	—	17
cis-(CH_3) Cl Pt [P $(C_2H_5)_3]_2$	»	113—116	17	37	—	17
trans-CH_3 (SCN) Pt[P$(C_2H_5)_3]_2$	»	93—95	17	37	—	17
trans-$(C_6H_5)_2$ Pt [As $(C_2H_5)_3]_2$	»	138—141	17	—	—	17
trans-(o-Tolyl)$_2$ Pt [P $(C_2H_5)_3]_2$	»	192—196	17	—	—	17
cis-(Metsityl) BrPt [P $(C_2H_5)_3]_2$	»	182—185	17	—	—	17
trans-$(CH{\equiv}C)_2$ Pt [P $(C_2H_5)_3]_2$	»	62—63	17	—	—	17
trans-$(C_6H_5C{\equiv}C)_2$ Pt [P $(C_2H_5)_3]_2$	»	186—187 (decomp.)	17	—	—	17
CH_3COPt (Cl) [P $(C_2H_5)_3]_2$	pale yellow	70—71	38	38	—	38
C_6H_5COPt (Cl) [P $(C_2H_5)_3]_2$	ditto	87—89	38	38	—	38
trans-$(CH_3)_2$ Pd [P $(C_2H_5)_3]_2$	–	—	41	—	—	—
trans-CH_3 (Br) Pd [P $(C_2H_5)_3]_2$	white	73—74	41	—	—	—
trans-$(C_6H_5)_2$ Pd [P $(C_2H_5)_3]_2$	—	95 (decomp.)	41	—	—	—
$[(CH_3)_2$ $NC_6H_4]_2$ Pd [P $(C_2H_5)_3]_2$	—	99—100	41	—	—	—
trans-$(C_6H_5C{\equiv}C)_2$ Pd [P $(C_2H_5)_3]_2$	—	164—166	41	—	—	—

TABLE 1 (contd).

Derivative*	Colour	M.p., °C	Reference			
			preparation	infrared spectra	NMR	dipole moment
CH_3CO (Cl) Pd [P $(C_2H_5)_3]_2$	pale yellow	65—67	38	38	—	38
(Bipyridyl) Pd $(n\text{-}C_3H_7)_2$	ditto	180—181	50	50	—	—
(Bipyridyl)Pd (CH_3) $(n\text{-}C_3H_7)$	yellow	206—207 (decomp.)	50	50	—	—
$(C_6H_5)_2$ Ni [P $(C_2H_5)_3]_2$	pale yellow	125—130 (decomp.)	43	—	—	—
(Mesityl)$_2$ Ni [P $(C_2H_5)_3]_2$	ditto	148—150 (decomp.)	43	—	—	42
(*o*-Tolyl)(Cl) Ni [P $(C_2H_5)_3]_2$	orange-red	75—77.5	43	—	—	43
(Mesityl)) (Br) Ni [P $(C_2H_5)_3]_2$	cinnamon brown	159—160	42,43	—	—	42,43
(C_6Cl_5) (Cl) Ni [P $(C_2H_5)_3]_2$	ditto	156—158	43	—	—	42,43
(Naphthyl)(Br) Ni [P $(C_2H_5)_3$]	»	150—152.5 (decomp.)	43	—	—	—
trans-$(HC\equiv C)_2$ Ni [P $(C_2H_5)_3]_2$	pale yellow	36—36,5	42,43	—	—	42
trans-$(C_6H_5C\equiv C)_2$ Ni [P $(C_6H_5)_3]_2$	orange	170—172 (decomp.)	42,43	—	—	42,43
CH_3 Ni (CO) C_5H_5	—	—	48	48	—	—
CH_3Ni [P $(C_6H_5)_3$] C_5H_5	dark green	115—118 (decomp.)	45	—	45	—
C_2H_5Ni [P $(C_6H_5)_3$]C_5H_5	ditto	90—110 (decomp.)	45	—	45	—
C_6H_5Ni [P $(C_6H_5)_3$] C_5H_5	»	137—139	45	—	—	—
$HC\equiv CNi$ [P $(C_6H_5)_3$] C_5H_5	»	111.5—112.5	45	45	—	—
$C_6H_5C\equiv CNi$ [P $(C_6H_5)_3$] C_5H_5	»	135	45	45	—	—
$(C_6F_5)_2$ Ni [P $(C_2H_5)_3]_2$	pale yellow	213--214	47	47	—	—
$(C_6F_5)_2$ Ni (bipyridyl)	dark yellow	255 (decomp.)	47	47	—	—
(C_6F_5) (Br) Ni [P $(C_6H_5)_3]_2$	yellow	199—200 (decomp.)	47	47	—	—
(C_6F_5) (SCN) Ni [P $(C_6H_5)_3]_2$	»	149—150	47	47	—	—
(C_6F_5) (I) Ni [P $(C_6H_5)_2$ $CH_3]_2$	red-brown	(decomp.)>260	46	—	—	—
$(n\text{-}C_3F_7)$ (I) Ni [P $(C_6H_5)_2$ $CH_3]_2$	ditto	220—222 (decomp.)	46	—	—	—
CF_3Ni (CO) C_5H_5	red	liquid	48	48	48	—
C_6F_5Ni (CO) C_5H_5	purple	»	48	48	48	—
$n\text{-}C_3F_7$Ni (CO) C_5H_5	»	»	48	48	48	—
CF_2=CF—CF_2Ni (CO) C_5H_5 + + CF_3—CF=CFNi (CO) C_5H_5	dark red	»	48	—	48	—
C_6F_5Ni [P $(C_6H_5)_3$] C_5H_5	dark green	164—165	48	48	48	—
CF_2=CF—CF=CFNi [P $(C_6H_5)_3$] C_5H_5	ditto	114—115	48	48	48	—

* Because of the number of complexes involved, no attempt has been made to rearrange the formulae in the tables into the IUPAC form (Ed. of Translation).

relation to the transition metals this is expressed in their ability to displace some of the carbonyl groups or carbonyl complexes from carbonyls or carbonyl complexes just as elemental iodine does. This reaction, which occurs under exceptionally mild conditions, is one of the methods of making perfluoroalkyl derivatives of transition metals (Method A). McBride and his coworkers[46] used it for nickel; they obtained iodo(perfluoroalkyl)nickel complexes containing the desired diphosphines, as diamagnetic crystals with a square-planar arrangement of the ligands — examples of complexes in which the effective atomic number rule is not obeyed. Nevertheless they are stable substances, with decomposition temperatures > > 200°, which is very remarkable considering that the analogous alkyl derivatives are incapable of existence:



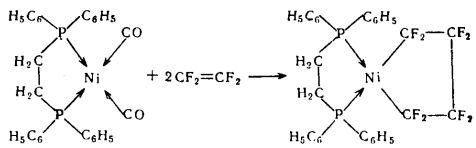
The perfluoroaryl complexes $NiAr_{f2}(PR_3)_2$ and $NiXAr_f.(PR_3)_2$ are stable even in solution[47]. Many of them

melt without decomposition and can be melted a second time.

Dimeric cyclopentadienylcarbonylnickel also decomposes readily under the action of perfluoroalkyl iodides, to form cyclopentadienylperfluoroalkylcarbonyl complexes[48]:

$$[Ni(C_5H_5)(CO)]_2 + R_fI \xrightarrow[25^\circ]{\text{benzene}} Ni(C_5H_5)R_f(CO) + NiI(C_5H_5)(CO).$$

Carbonyls and carbonyl complexes of some metals react with perfluoroethylene, some of the carbonyl groups being replaced. The expected π complexes are not formed, however, but σ heterocycles with the metal atom in the ring. This is one of the methods of obtaining stable perfluorinated σ derivatives of nickel, cobalt, and iron (Method B)[49]:



Single examples of perfluoroalkyl derivatives of platinum and palladium are known. Thus in the treatment of bipyridyldimethylpalladium with perfluoropropyl iodide replacement of one or both of the methyl groups occurs[50]:

$$Pd(C_{10}H_8N_2)(CH_3)_2 + CF_3CF_2CF_2I \xrightarrow[20^\circ]{\text{tetrahydrofuran}} Pd(C_{10}H_8N_2)(C_3F_7)_2.$$

There is a reference to the bis(perfluoroethyl)platinum complex $Pt(C_2F_5)_2\{P(C_2H_5)_3\}$ obtained by the addition of perfluoroethylene to a fluoro-complex in hydrogen fluoride medium[10].

The example of nickel is a clear, convincing illustration of the stabilising influence of fluorine on the transition metal–carbon σ bond.

Iron, ruthenium, osmium. Numerous attempts to bring about reaction between a Grignard reagent and iron(II) or iron(III) halides have ended in the reduction of the metal and the formation of the dimer of the radical of the arylating agent:

$$2MgBr(C_6H_5) + FeCl_2 \rightarrow C_6H_5C_6H_5 + Fe + MgBr_2 + MgCl_2.$$

The dimerisation was subsequently used as a method of preparation, and, as is well known, one of the two discoveries of ferrocene is connected with an attempt to obtain biscyclopentadienyl from bromo(cyclopentadienyl)-magnesium and iron(III) chloride. On the other hand this reaction was considered to be a measure of the stability of the σ derivative formed as an intermediate and all the metals of Group VIII have been studied from this viewpoint in terms of reaction with phenylmagnesium bromide[27,51]. When the yield of biphenyl is taken as a measure of the instability of the σ derivative, then it must be concluded that the phenyl derivatives of iron, cobalt, nickel, ruthenium, rhodium, and palladium are evidently completely unstable and exist only briefly. As shown above, platinum gives stable methyl derivatives. Probably its phenyl derivatives are also fairly stable, since under comparable conditions only traces of biphenyl are formed. The low yield of biphenyl is also found with osmium(III) and iridium(III) chlorides, and their phenyl derivatives evidently exhibit moderate stability. The catalytic reaction of dimerisation, which takes place in the presence of non-stoichiometric amounts of transition metal salt, was studied by Kharasch and coworkers[52-56], and it was shown that $CoCl_2$ exhibits the greatest activity of them all. The mechanisms advanced for different types of R took into account the strength of the metal–carbon bond in the hypothetical MR_n.

Subsequently the formation of unstable derivatives in the first stage was used in the original synthesis of π alkene complexes by Fischer and coworkers[57-60], for example:

$$FeCl_3 + 3MgBrPr^i \xrightarrow{\text{ether}} [FePr^i_3(\text{ether})_n] \xrightarrow[35^\circ,\ \text{ultraviolet}]{2C_6H_8} \pi\text{-}C_6H_8FeC_6H_8\text{-}\pi + C_3H_8 + C_3H_6 + H_2.$$

The labile ethereal complex of triisopropyliron decomposes when irradiated and the vacated coordination sites are occupied by the alkene. If the geometrical or electronic properties of the alkene structure do not match up to the metal then there is a simultaneous rearrangement of the alkene, in the present example dehydrogenation. In this way otherwise unobtainable pure alkenic π complexes of iron, ruthenium, osmium, and chromium of low stability were prepared.

The polymerisation of acetylene in the presence of derivatives of chromium, nickel, etc. is apparently brought about by an analogous mechanism. Hence because of their reactivity the unisolable, unstable σ derivatives of the transition metals play an important part in the intermediate stages of many processes.

In addition to these organic derivatives of iron, ruthenium, and osmium, which apparently exist in solutions but cannot be isolated pure, several completely stable mixed complexes have been obtained. For iron there are first of all derivatives of cyclopentadienyldicarbonyliron and corresponding dinuclear complexes, some tetracarbonyl-complexes and their fluorinated analogues and also complexes of the MR_2L_2 type, although the last are evidently the least characteristic. For ruthenium and osmium only the four-coordinated complexes of composition $MXRL_2$ are known.

Derivatives of cyclopentadienylcarbonyls are obtained by two main methods (C) and (D), developed by Piper and Wilkinson[61]:

$$\left.\begin{array}{l} C_5H_5M(CO)_nNa + RCl \\ MX(C_5H_5)(CO)_n + MgXR \end{array}\right] \rightarrow M(C_5H_5)R(CO)_n \qquad \begin{array}{l}\text{(Method C)}\\ \text{(Method D)}\end{array}$$

A method which has limited application for obtaining only methyl derivatives is the methylation of hydro(cyclopentadienyl)carbonyl complexes with diazomethane[61,62]:

$$C_5H_5M(CO)_nH + CH_2N_2 \rightarrow C_5H_5M(CO)_nCH_3 + CO. \qquad \text{(Method E)}$$

Method C forms the basis of the preparation of dinuclear complexes[63,64], dihalides being used. Acyl and fluorocarbon derivatives are also obtained by Method B. It has been shown that trimethylsulphonium iodide can be used as a methylating agent in Method B.[65] The yields in all three methods vary considerably. Table 2 gives the physical properties of some representatives of this class of complexes. Usually the isoalkyl derivatives are considerably less stable than the n-alkyl. Many of these are liquids which are readily oxidised even at low temperatures.

The following methods for obtaining σ alkyl and aryl derivatives involves the decarbonylation of the corresponding σ acyl derivatives:

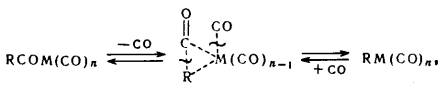
$$M(RCO)(C_5H_5)(CO)_n \rightarrow MR(C_5H_5)(CO)_n + CO. \qquad \text{(Method F)}$$

TABLE 2. σ derivatives of iron, ruthenium, and osmium.

Derivative	Colour	M.p., °C	Reference			
			preparation	infrared spectra	NMR	dipole moment
$(C_6Cl_5)_2$ Fe [P $(C_6H_5)_3$ $C_6H_5]_2$	yellow	135—142 (decomp.)	72	—	—	—
CH_3Fe $(CO)_2$ C_5H_5	»	78—82	61,65	61	61	—
C_2H_5Fe $(CO)_2$ C_5H_5	»	liquid	61	61	61	—
σ-C_6H_5Fe $(CO)_2$ C_5H_5-π	orange	46	61	61	61	—
C_6H_5Fe $(CO)_2$ C_5H_5	yellow	35—36	61,69	61,69	61,69	—
CH_2=$CHFe$ $(CO)_2$ C_5H_5	orange	liquid	69	69	69	—
HC≡CCH_2—Fe $(CO)_2$ C_5H_5	orange-red	96—96.5	188	188	188	—
CH_2=CH—CH_2—Fe $(CO)_2$ C_5H_5	amber	b.p. $45/10^{-3}$	68	68	68	—
n-C_3H_7—Fe $(CO)_2$ C_5H_5	»	liquid	186	186	186	—
$(CH_3)_2$ CD—Fe $(CO)_2$ C_5H_5	—	—	186	186	186	—
$(CH_3)_3$ C—Fe $(CO)_2$ C_5H_5	yellow	liquid	186	186	186	—
		decomp. >20				
CNCH_2Fe $(CO)_2$ C_5H_5	orange-yellow	123	190	190	190	—
CNCH_2CH_2Fe $(CO)_2$ C_5H_5	ditto	29.5	190	190	190	—
CH_3CH (CN) Fe $(CO)_2$ C_5H_5	orange-red	86—87	190	190	190	—
CH_3OOC—(C=C)—$COOCH_3$ Fe$(CO)_4$	yellow-orange	57	71	—	71	—
$(CH_2)_3$ [Fe $(CO)_2$ $C_5H_5]_2$	orange	103—135	63	63	63	—
CH_3C≡CCH_2 [Fe $(CO)_2$ $C_5H_5]_2$	»	—	63	63	63	—
CH_3COFe $(CO)_2$ C_5H_5	»	56—57	64	64	64	—
C_2H_5COFe $(CO)_2$ C_5H_5	orange-red	liquid	67	67	67	—
C_6H_5COFe $(CO)_2$ C_5H_5	orange	59—62	69	69	69	—
CH_2=$CHCOFe$ $(CO)_2$ C_5H_5	»	liquid	69	69	69	—
$(CH_3)_2$ NCO—Fe $(CO)_2$ C_5H_5	»	111—112	64	64	64	—
CO $(CH_2)_3$ CO [Fe $(CO)_2$ $C_5H_5]_2$	»	110—111.5	64	64	64	—
CF_3Fe $(CO)_4$ I	orange-red	94 (decomp.)	74	74	—	—
C_2F_5Fe $(CO)_4$ I	dark red	15—16	74	21,74	81,69	—
C_6F_5Fe $(CO)_4$ I	ditto	74	77	77	—	—
[C_2F_5Fe $(CO)_2$ I]$_2$	»	110—112 (decomp.)	74	74	—	—
[C_3F_7Fe $(CO)_2$ I]$_2$	pale orange	140—142 (decomp.)	74	74	—	—
$(CF_2)_4$ = $Fe(CO)_4$	white	77	21,80	21	21	—
$(C_2F_5)_2$ $Fe(CO)_4$	pale yellow	62—63.5	74,75	74	81,69	—
(n-$C_3F_7)_2$ Fe $(CO)_4$	ditto	88—89	74	74	81,69	—
n-C_3F_7Fe $(CO)_3$ (I) P $(C_6H_5)_3$	pale brown	125 (decomp.)	82	82	—	—
n-C_3F_7Fe $(CO)_3$ (I) (pyridine),	cinnamon brown	123	82	82	—	—
(n-$C_3F_7)_2$ Fe $(CO)_2$ (pyridine),	pale brown	138	82	82	—	—
CF_3Fe $(CO)_2$ C_5H_5	pale yellow	137—139	69	69	69	—
C_2F_5Fe $(CO)_2$ C_5H_5	orange	43—45	69	69	69	—
CF_3CF=$CFFe$ $(CO)_2$ C_5H_5	yellow-orange	69.5—70.5	74,75,76	74, 76	74, 76	—
$(CF_2)_3$ [Fe $(CO)_2$ $C_5H_5]_2$	yellow	168—172	75	—	—	—
C_6F_5Fe $(CO)_2$ C_5H_5	yellow-orange	144.5—145	78,79	79	78,79	—
p-HC_6F_4Fe $(CO)_2$ C_5H_5	»	128—130	79	79	79	—
p $CF_3C_6F_4Fe$ $(CO)_2$ C_5H_5	ditto	119—120	79	79	79	—
CF_3COFe $(CO)_2$ C_5H_5	orange	33—34	69	69	69	—
C_2F_5COFe $(CO)_2$ C_5H_5	»	liquid	69	69	69	—
CO $(CF_2)_3$ CO [Fe $(CO)_2$ $C_5H_5]_2$	»	112—113	64	64	64	—
C_2H_5CORu $(CO)_2$ C_5H_5	pale yellow	liquid	67	67	67	—
CH_3 (H) Ru [CH_3P $(C_6H_5)_2]_2$	colourless to pale yellow	(decomp.)	73	73	—	—
C_3H_7 (H) Ru [$CH_2P(C_6H_5)_2]_2$	colourless to pale yellow	120—220	73	73	—	—
CH_3 (Cl) Ru [CH_2P $(C_6H_5)_2]_2$	—	312 (decomp.)	18,73	—	—	18
C_2H_5 (Cl) Ru [CH_2P $(C_6H_5)_2]_2$	—	330 (decomp.)	18,73	—	—	18
CH_3 (Cl) Os [CH_3P $(C_6H_5)_2]_2$	—	295—296 (decomp.)	18	—	—	18
C_2H_5 (Cl) Os [CH_2P $(C_6H_5)_2]_2$	—	310—314 (decomp.)	18	—	—	18

This method is widely used in the chemistry of the carbonyl complexes of manganese and cobalt, where the acyl derivatives are more accessible than the alkyl derivatives. The decarbonylation of manganese and cobalt acylcarbonyls proceeds very easily on heating. It is often so easy that even at room temperature and normal pressure an equilibrium mixture of the alkyl and acyl derivatives is formed. However, when there is only one phosphine or cyclopentadienyl group in the complexes then the decarbonylation is greatly hindered. Thus although a series of acyl derivatives of cyclopentadienyldicarbonyliron was obtained[64,66,67], they could not be decarbonylated just so long as the change from σ allyl to π allylcyclopentadienylcarbonyl complexes did not succeed[68].

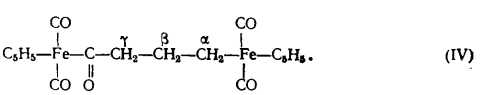
Radiochemical methods were used to show[66] that the reversible carbonylation–decarbonylation process takes place by the mechanism:



that is, it is not the acyl carbonyl that is detached, but one of the CO groups of the carbonylmetal moiety. The reverse reaction of carbonylation of the alkyl complex proceeds in such a way that the CO entering bonds only with the metal, and the acyl group is formed by an inner-sphere rearrangement. Therefore the success of the decarbonylation of acylcarbonyls probably depends on how strongly the carbonyl groups of such complexes are bound to the metal, which can be judged from the ease with which they are replaced by a phosphine. King and Bisnett found[69] that decarbonylation of acyls is facilitated by ultraviolet irradiation, just as the replacement of CO by phosphine is sometimes facilitated. A synthesis path was worked out for certain previously inaccessible alkyl complexes, for example, cyclopentadienylvinyldicarbonyliron. All this relates also to cyclopentadienylperfluoroacyl complexes. They are obtained by Method C; when the acyl halides are gaseous, the anhydrides of the perfluoro-acids are used. The yields of perfluoroacyls are usually about 10% low and in the reactions a large quantity of the dimer of cyclopentadienyldicarbonyliron is always obtained. Acyl derivatives of unsaturated acids also give low yields.

It has been repeatedly noted[64,69] that in the nuclear magnetic resonance spectra of the complexes $FeR(C_5H_5)(CO)_2$ the position of the signals of the ring protons depends on the nature of R. Thus when R = alkyl it is $\sim 5.27\ \tau$, with R = acyl $\sim 5.17\ \tau$, with R = perfluoroacyl $\sim 5.04\ \tau$, and with R = I 4.93 τ, that is, the displacement varies inversely with the electronegativity of R. The shifts for ring protons in fluoroalkyls and fluoroacyl complexes are very similar.

The displacements for the α and β protons of an alkyl chain are almost the same, that is, by the NMR method it is impossible to distinguish them



(IV)

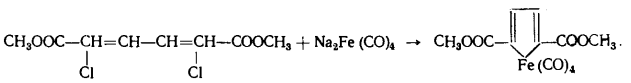
In the acyl groups two types of protons are evident, corresponding to the γ and β positions. Non-symmetrical doubly-charged complexes of type (IV) have two ring proton signals associated with the different electronegativity of the groups attached to the iron.

Quite recently a new reaction between the σ complexes of iron with liquid SO_2 was discovered. Analogously to carbon monoxide, SO_2 is inserted at the R–Fe bond. The reaction proceeds easily at -40° to -60° immediately the complex is dissolved in liquid SO_2:[70]

$$Fe(C_5H_5)R(CO)_2 + SO_2 \rightarrow Fe(C_5H_5)(SO_2R)(CO)_2,$$

where R = CH_3, C_2H_5, or C_6H_5.

A derivative of the so-called ferrole — a five-membered unsaturated heterocycle with iron in the ring — is obtained by the reaction of dihalogenoalkenes with $Na_2Fe(CO)_4$:[71]



It is crystalline, m.p. 57°, and capable of being chromatographed under the usual conditions.

The ferrole motiv is repeated in a series of complexes obtained from iron carbonyls and alkynes, which will be considered below.

Hydro-complexes are capable of addition to alkenes, and this reaction is one of the paths for the synthesis of σ derivatives (Method G). In the group of metals now being considered addition to the butadiene system takes place:[68]

$$FeH(C_5H_5)(CO)_2 + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Fe(CH_2{-}CH{=}CH{-}CH_3)(C_5H_5)(CO)_2.$$

The sole example of a four-coordination iron complex — bis(pentachlorophenyl)bis(diethylphenylphosphine)-iron — is crystalline, with decomposition temperature $\sim 130°$.[72] The analogous complexes of ruthenium and osmium usually contain only one alkyl group and a halogen atom, which can be reduced and the corresponding hydro(alkyl) complexes obtained. Unlike all the others, the square complexes of ruthenium and osmium are obtained by the action of trialkylaluminium on dihalogeno--complexes[73]. Judging by the decomposition temperature, the least stable complexes of this group are those of iron.

It was shown above that perfluoroalkyl halides displace the carbonyl groups in carbonyl complexes of nickel. Pentacarbonyliron also reacts under mild conditions at 25–70° with perfluoroalkyl halides, giving a mixture of derivatives of composition $FeIR_f(CO)_4$ and $[FeIR_f(CO)_3]_2$.[21,74] The latter is dimerised by means of halogen bridges. On heating, the monomeric complexes lose CO, being converted into dimers.

Unlike the cyclopentadienylperfluoroacylcarbonyls, which are decarbonylated only under ultraviolet irradiation[64,69], perfluoroacylcarbonyls of iron are decarbonylated apparently quite readily, since when perfluoroacyl chlorides and $Na_2Fe(CO)_4$ react, only bisperfluoroacylcarbonyls can be isolated[74,75]. In this respect they are more similar to the acyl derivatives of cobalt and manganese. It should be noted, however, that the replacement of even one of the carbonyl groups by a phosphine makes the acyl derivatives stable to thermal decarbonylation. Decarbonylation of perfluoroacyl derivatives gave complexes of the type $Fe(C_5H_5)R_f(CO)_2$,[69] with different R_f, shown in Table 2. Some of these can also be obtained by Method C[74,76] (see p. 173). The perfluoroaryl complexes are obtained with yields of 2–7% by the action of pentafluorophenyllithium[77] or bromo(pentafluorophenyl)magnesium[78] on the corresponding halogen derivatives.

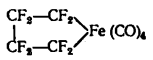
Nucleophilic replacement of fluorine by other groups is characteristic for highly fluorinated aromatic hydrocarbons. King and Bisnette[79] used this feature to obtain fluorinated aromatic σ derivatives of iron. On heating fluorobenzenes in tetrahydrofuran with $Na[Fe(C_5H_5)(CO)_2]$, fluorine is replaced by the cyclopentadienyl dicarbonyliron cation:

$$C_6F_5R + Na[Fe(C_5H_5)(CO)_2] \rightarrow [Fe(C_5H_5)(p\text{-}RC_6F_4)(CO)_2],$$

where R = H, or CF_3.

With octafluorotoluene in this reaction, fluorine is displaced from the benzene nucleus, not the side-chain, 1,2,3,4-tetrafluorobenzene gives $[Fe(C_5H_5)(2,3,6\text{-}C_6H_2F_3).(CO)_2]$ that is, the C–Fe bond is bound in such a way that both *ortho*-positions are occupied by fluorine. The yields in these reactions reach 30–50%, but the method is not applicable to $Na_2[Fe(CO)_4]$, $Na[Mo(C_5H_5)(CO)_3]$, and some other carbonylmetalates. The complexes obtained are stable on heating and against oxidation, melt without decomposition, and can be chromotographed on Al_2O_3.

Yet another type of iron complexes — heterocyclic complex (V), obtained by Method B[21,80] originally was thought to be a π perfluoroethylene complex — is the substance



(V)

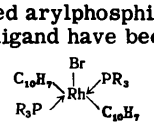
stable in all respects.

It is not decomposed by bromine, phosphines do not displace the perfluorohydrocarbon and only prolonged thermal treatment (120 h at 70°) leads to the detachment of perfluorocyclobutane.

As Table 2 shows, fluorocarbon complexes do not differ from the hydrocarbon analogues in ability to exchange ligands. One or two of their carbonyl groups can be replaced by phosphines or amines[82]. NMR data for the fluorocarbon complexes have been given by Pitcher and coworkers[81].

Cobalt, rhodium, iridium. It has been reported[83,84] that organometallic derivatives of the composition $CoX_3(C_{10}H_7)$ and $CoX_2(C_{10}H_7)_2$ are obtained by the action of halogeno(naphth-2-yl)magnesiums on ethereal solutions of cobalt salts. But since data about their composition, hydrolysis products, and thermal decomposition are insufficient, it is impossible to consider the existence of the simplest σ derivatives of cobalt as proved. Those classes of derivatives which contain carbonyls or phosphines, etc. instead of σ groups have been more thoroughly studied. Quite recently a new class of stable organic derivatives was discovered — the alkylpentacyanocobaltates. Perfluorinated analogues of some of these complexes have been obtained. Cobalt, like the other elements of Group VIII, is capable of forming four-coordinated complexes of *trans*-configuration $CoAr_2L_2$, where Ar is a bulky aromatic radical of the mesityl type[72]. They are all crystalline and melt with decomposition above 100°. They are somewhat less stable than the analogous derivatives of Pt, Pd, and Ni, which Chatt explains by a tetrahedral (instead of planar) arrangement of the ligands. The stabilising action of the phosphine groups is less in such a configuration.

Five-coordinated arylphosphine complexes (VI), having halogen as a fifth ligand have been obtained for rhodium[85]:

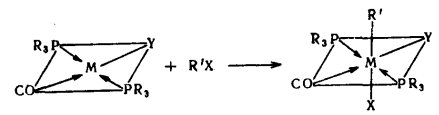


(VI)

In these compounds the rhodium(III) — usually six-coordinated — is coordinatively unsaturated and it could be expected that these substances would be unstable towards nucleophilic attack; however, they are completely stable. This is explained by the almost spherical structure formed by the bulky ligands which compactly surround the metal and shield it from the attacking agent.

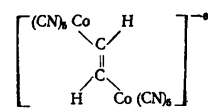
A preliminary communication that complexes of the type MR_2L_2 are obtained has been published[18].

Six-coordinated σ complexes of iridium(III) and rhodium(III) have been obtained[86]. They are formed as a result of the addition of active organic halides to some planar complexes of iridium(I) and rhodium(I):



During this, the metal is oxidised to the tervalent state. Table 3 lists some of the complexes obtained in this way. They are all crystalline, high-melting materials, stable in air.

Griffith and Wilkinson[87] observed, as long ago as 1959, that aqueous solutions of a pentacyanocobaltate absorb acetylene. They isolated a crystalline, diamagnetic salt of composition $K_6[Co_2(CN)_{10}(C_2H_2)].4H_2O$, which has been ascribed the structure (VII) on the basis of infrared and NMR analyses:



(VII)

The *trans*-configuration was chosen arbitrarily, as there are no analogues for these compounds and the available data are insufficient to settle the question of configuration conclusively. It was later shown[88] that aqueous solutions of $[CoH(CN)_5]^{-3}$ and $[Co(CN)_5]^{-3}$ absorb perfluoroethylene at atmospheric pressure. Salts of the composition $K_3[Co(CN)_5(CF_2CF_2H)]$ and $K_6[(CN)_5Co(CF_2CF_2)Co(CN)_5]$ were isolated. Unlike (VII), which is of comparatively low stability, decomposes slowly in air and rapidly in a vacuum at 70°, the fluorinated complex salts are stable to oxidation and thermally up to 300°. The reaction with perfluoroethylene goes so easily and unambiguously, that, in the authors' opinion, it can be used analytically for determining metal–hydrogen bonds when the latter cannot be observed by NMR analysis.

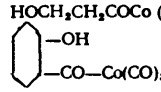
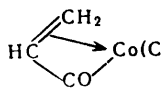
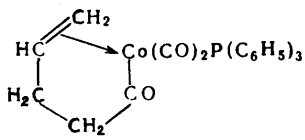
A variant of the synthesis of this class of complexes consists of the reactions of pentacyanocobaltates with alkyl halides[89]. It is possible to start from a mixture of $CoCl_2$ and NaCN:

$$2[Co(CN)_5]^{-3} + C_6H_5CH_2Br \rightarrow [Co(CN)_5(C_6H_5CH_2)]^{-3} + [CoBr(CN)_5]^{-3}.$$

Methyl, ethyl, and n-propyl derivatives are obtained analogously. The most stable of these are the benzyl complexes, which are slowly decomposed in air, split off bibenzyl when heated in a vacuum, and are decomposed by acids and mercury(II) chloride.

Many investigations have been devoted to acyl and alkyl derivatives of cobalt carbonyls. The interest in them is undoubtedly connected with explaining the mechanism of

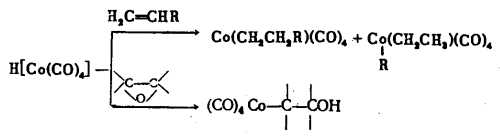
TABLE 3. σ derivatives of cobalt, rhodium, and iridium.

Derivative	Colour	M.p., °C	Reference			
			preparation	infrared spectra	NMR	dipole moment
$CH_3Co(CO)_4$	yellow	exists <—80	91,112	91,112	—	—
$C_6H_5Co(CO)_3P(C_6H_5)_3$	»	140	106	106	—	—
$CH_3COCo(CO)_4$	–	—	99	99	—	—
$C_6H_5COCo(CO)_4$	–	—	99	99	—	—
$HOCH_2CH_2COCo(CO)_3P(C_6H_5)_3$	yellow-brown	95—100 (decomp.)	93	93	—	—
	pale yellow	—	93	—	—	—
$CH_2=CHCH_2COCo(CO)_3P(C_6H_5)_3$	yellow	82(decomp.)	90	90	—	—
	»	106—107 (decomp.)	90	90	—	—
	slightly coloured	106.5—107	90	90	—	—
$CH_2=CH(CH_2)_3COCo(CO)_3P(C_6H_5)_3$	yellow-brown	90.5—93 (decomp.)	96	96	—	—
$(CH_3)_3COCOCo(CO)_3P(C_6H_5)_3$	—	(decomp.)>100	105	—	—	—
trans-(Mesityl)$_2$Co[P(C$_2$H$_5$)$_3$]$_2$	yellow	113—116 (decomp.)	72	—	—	—
trans-(2-$C_6H_4C_6H_5$)$_2$Co[P(C$_2$H$_5$)$_2$C$_6$H$_5$]$_2$	»	115—119 (decomp.)	72	—	—	72
trans-(2-Methyl-1-naphthyl)$_2$Co[P(C$_2$H$_5$)$_2$C$_6$H$_5$]$_2$	»	144—146 (decomp.)	42,72	—	—	42,72
trans-(C_6Cl_5)$_2$Co[P(C$_2$H$_5$)$_2$C$_6$H$_5$]$_2$	lemon-yellow	224—228 (decomp.)	72	—	—	45
$CF_3Co(CO)_4$	amber	13.31/28 mmHg	107,108	107,108	107	—
$C_2F_5Co(CO)_4$	»	b.p. 32/16 mmHg	106,107	106,107	107	—
$n\text{-}C_7F_{15}Co(CO)_4$	yellow-brown	30	106	106	—	—
$CF_3Co(CO)_3P(C_6H_5)_3$	pale yellow	168	108	108	—	—
$C_2F_5Co(CO)_3As(C_6H_5)_3$	dark yellow	134	106	106	—	—
$C_2F_5Co(CO)_3Sb(C_6H_5)_3$	yellow-brown	120	106	106	—	—
$C_2F_5Co(NO)_2P(C_6H_5)_3$	violet-brown	65	106	106	—	—
$(CO)_4CoCF_2CF_2Co(CO)_4$	orange	70 (decomp.)	80	80	80	—
$CF_3COCo(CO)_4$	yellow	4	108	108	—	—
$CF_3COCo(CO)_3P(C_6H_5)_3$	»	172	108	108	—	—
$C_2F_5COCo(CO)_3P(C_6H_5)_3$	»	138	106	—	—	—
$CF_3(I)Co(CO)C_5H_5$	black	145 (decomp.)	110	111	111	—
$n\text{-}C_3F_7(I)Co(CO)C_5H_5$	»	121	110	111	69,81	—
$(CF_3)_4=Co(CO)C_5H_5$	yellow	106	109	109	109	—
$(C_6F_5)_2Co[CH_2P(C_6H_5)_2]_2$	»	186 (decomp.)	47		—	—
$CH_3Rh(Cl)(I)(CO)[P(n\text{-}C_4H_9)_3]_2$	pale yellow	85—86	86	86	—	—
$C_6H_5CH_2Rh(Cl)(Br)(CO)[P(n\text{-}C_4H_9)_3]_2$	ditto	109—110.5	86	86	—	—
$CH_3CORh(I_2)(CO)[P(n\text{-}C_4H_9)_3]_2$	orange	76—78	86	86	—	—
(Naphth-1-yl)$_2$Rh(Br)[P(C$_3$H$_7$)$_3$]$_2$	white	137—139	85	—	—	85
$CF_3Rh(I)(CO)C_5H_5$	red	168—169	111	111	111	—
$C_2F_5Rh(I)(CO)C_5H_5$	»	145—147	111	111	111	—
$C_3F_7Rh(I)(CO)C_5H_5$	»	118—119	111	111	111	—
$CH_3Ir(Cl)(I)(CO)[P(C_6H_5)_3]_2$	pale yellow	268—269 (decomp.)	86	—	—	—
$CH_3OOCCH_2Ir(Cl)(I)(CO)[P(C_6H_5)_3]_2$	ditto	248—249	86	—	—	—
$CH_2=CHCH_2Ir(I_2)(CO)[P(C_6H_5)_3]_2$	red-brown	214	86	—	—	—

the oxo-synthesis. Alkylcarbonylcobalts can be obtained from alkyl halides and sodium carbonylcobaltates [90,91]:

$$Na[Co(CO)_4] + XR \rightarrow RCo(CO)_4, \qquad \text{(Method H)}$$

or by addition of hydrogen tetracarbonylcobaltate(-1) to alkenes [92] or epoxy-compounds [93,94]:



Alkylcobaltcarbonyls evidently exist in equilibrium with an acyl form. This is suggested

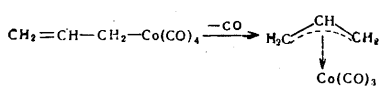
$$RCo(CO)_4 \rightleftarrows RCOCo(CO)_3 \overset{CO}{\rightleftarrows} RCOCo(CO)_4$$

by the existence of a 5.8 μ band in the spectra of alkylcarbonyls in the gas phase and in solutions. The ease of the reciprocal changes and the instability of one or the other often does not allow them to be isolated in a pure state. This applies especially to the alkylcarbonyls. Irrespective of the nature of R they can be characterised only in the form of acylcarbonylphosphine complexes. This is because during the treatment of the alkylcarbonyl with phosphine the CO being displaced does not depart to the outer sphere, but is inserted at the R–Co bond, with formation of an acyl complex:

$$RCo(CO)_4 + PR'_3 \rightarrow RCOCo(CO)_3PR'_3.$$

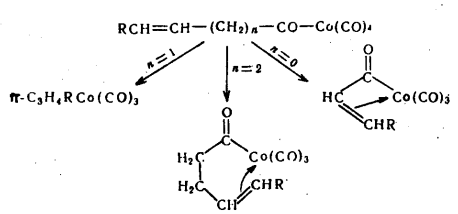
Hence the acyl complex is obtained directly by Method H in the presence of phosphines.

When R is an unsaturated radical the molecule is stabilised by rearrangement into a π complex. For example, the stage of the σ allyl derivative could not be isolated since on heating it is converted into the π allylcarbonyl [90,95]:



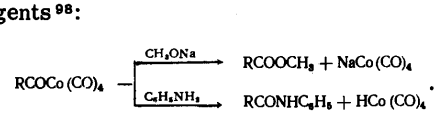
The special nature of the bond in a π allyl complex makes it incomparably more stable compared with the σ complex, although in either the metal has a closed electron configuration of krypton and the same stabilising ligands. When phosphines act on it, one of the carbonyl groups is replaced, but acyl complexes are not thus obtained.

Acylcarbonyls of cobalt are obtained by the carbonylation of alkylcarbonyls or by Method H. When the acyl radical has an unsaturated chain, reaction H takes place with liberation of CO, but the products obtained contain an acyl group. It is thought that one of the CO groups of the carbonyl residue is displaced by the carbon–carbon double bond and a $\sigma\pi$ complex is obtained:



The intermediate acyltetracarbonyl complexes are not usually isolated, but sometimes their crystalline phosphine derivatives can be obtained [90,96,97].

The acylcarbonyls readily react with various nucleophilic reagents [98]:

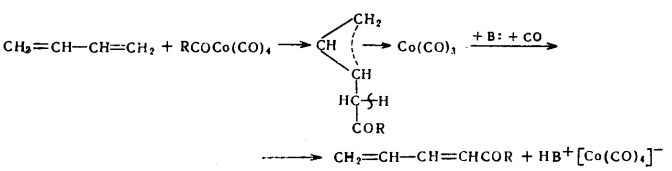


Like the alkyl compounds they are extremely unstable thermally. Thus methyltetracarbonylcobalt exists as yellow crystals at -80° and decomposes at higher temperatures, but the acyltetracarbonylcobalt is a crystalline substance with m.p. -33° and decomposition temperature -20°. The combination of the properties described for the acyl and alkyl derivatives of cobalt carbonyl determines their role in catalytic processes, and in turn in hydroformylation.

Analogous syntheses and transformations are also possible for manganese carbonyl. Here also the reversible reaction of carbonylation–decarbonylation is characteristic, but both the alkyl and the acyl derivatives of manganese carbonyl are considerably more stable and can be isolated.

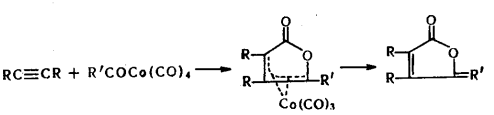
Phosphines replace one of the carbonyl groups of acyl complexes [98-100]. Some sterically strained tertiary phosphites are capable of displacing one, two, and even three carbonyl groups, but the phosphito(acyl) complexes thus obtained are unstable to oxidation [101].

Heck [102-104] observed an interesting ability of acylcarbonyls to add to a diene system or acetylene. With the former, substituted π allylcarbonyls are obtained, which under the action of nitrogenous bases decompose with the liberation of acyldienes:



Since the acyl complex is always found in equilibrium with the alkyl, the same result is obtained on starting from the alkylcarbonyls, or what is even simpler, on taking a mixture of the sodium salt of a carbonyl, an alkyl halide, diene, and amine.

The addition of acylcarbonyls to the acetylenes leads to a complex type of π-enyl, the formation of which is confirmed spectroscopically, and also the liberation of phosphine derivatives. An intermediate complex, by breaking down in the presence of amine, gives an unsaturated lactone:



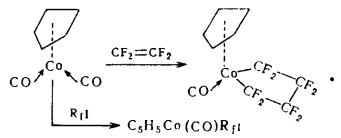
Some examples are known of perfluoroalkylcarbonyl-cobalt complexes, obtained by Method H [106-108] (see above). In attempts to use this method to obtain perfluoroacylcarbonyls, decarbonylation took place simultaneously. However, when the reaction is carried out below room temperature perfluoroacylcarbonyls can be isolated [106,108]. If then one of their carbonyl groups is replaced by a phosphine, then acyl derivatives completely stable to decarbonylation are obtained [106,108]. Both types of σ complex are considerably more stable than their hydrocarbon

analogues. It should be noted that the back reaction of carbonylation of the perfluoroalkylcarbonyls evidently occurs with greater difficulty than for the alkylcarbonyls, since during reaction with phosphines, arsines, or stibines CO is liberated and an acyl complex is not obtained.

Cobalt carbonyl in tetrahydrofuran under very mild conditions at room temperature reacts with perfluoroethylene, which is inserted between the two metal atoms, giving a dinuclear σ complex[80]:

$$Co_2(CO)_8 + CF_2{=}CF_2 \rightarrow (CO)_4CoCF_2CF_2Co(CO)_4.$$

Under somewhat more severe conditions, in an autoclave at 160° perfluoroethylene reacts with cyclopentadienyldicarbonylcobalt, one of the carbonyl groups being replaced by a perfluorinated ring[109]:

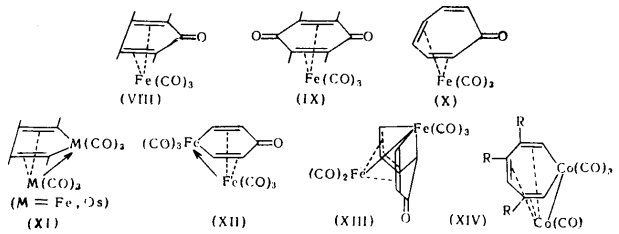


Finally, one of the carbonyl groups can be displaced by a perfluoroalkyl iodide[110]. Cyclopentadienyldicarbonylrhodium behaves analogously[111].

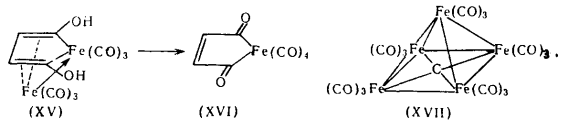
Table 3 contains some examples of σ complexes of cobalt. rhodium, and iridium.

Products of the reaction of alkynes with carbonyls and carbonyl complexes of Group VIII metals. Diels–Alder type of metal addition. The variety of complexes obtained from acetylenes and carbonyls or carbonyl complexes may be recalled again. Although the structure of many of these is not indisputable, continuing study of them led to an interesting hypothesis and paths for future investigation were noted.

Acetylene, as such, hardly ever participitates in the formation of π complexes, although acetylenic π complexes are evidently the first stage in the reaction and can be isolated when platinum is involved. Among the products of the reaction of iron and cobalt carbonyls with acetylene, two classes of derivatives (in addition to others) have been isolated: (1) carbonyl complexes of unsaturated ketones, obtained as the result of the cyclic polymerisation of several acetylene molecules, with the participation of carbon monoxide, (VIII), (IX), (X), etc.; (2) five-, six-, and seven-membered heterocycles with metal atoms in the ring (XI), (XII), (XIII), (XIV)[113-119]. For the structure of (XIV), however, see Mills and Robinson[120].

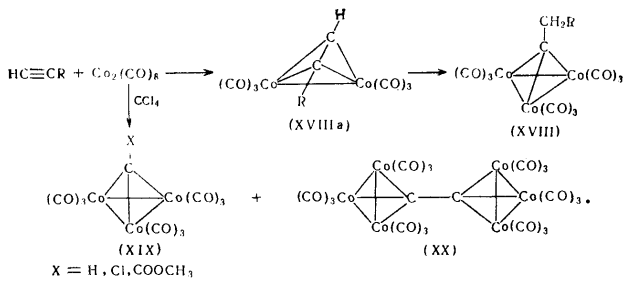


The formation of heterocycles is thus brought about by σ bonding with the metal. The molecules are stabilised by the attachment of a second carbonylmetal grouping of the π complex formation type. Their structure was confirmed by chemical destruction and also by X-ray analysis. Most of them are sufficiently stable thermally to be isolated in a pure state. The chemical stability is confirmed by such facts as, for example, the possibility of replacing the CO groups by other ligands, in particular, SO_2 [121], or by the oxidation (XV) → (XVI) with retention of the ring structure[122]:



The reaction of $Fe_3(CO)_{12}$ with some substituted acetylenes leads to the formation of (XVII) together with other complexes. The substance is diamagnetic, does not have bridging CO groups, and X-ray structural analysis has shown it to be a tetragonal pyramid at the apices of which tricarbonyliron groups are situated, and a single carbon atom lies in the base of the pyramid[123].

The analogous carbide-like compounds (XVIII), (XIX), and (XX) (if the carbon of the CO groups is not considered) are also obtained from octacarbonyldicobalt and monosubstituted acetylenes[114,124,125] carbon tetrachloride, or bromoform[126]:

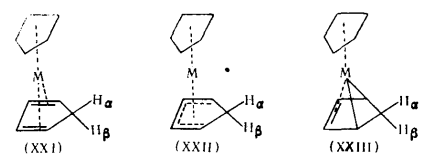


Structures of type (XVIIIa) have been proposed for the products of the reaction of $Hg[Co(CO)_4]_2$ and disubstituted acetylenes[127,128] and also for some derivatives of cyclopentadienylcarbonylnickel[129]. All are crystalline, often deeply coloured substances, sometimes with high melting points (~ 200°) and stable in air.

Hence the transition metal–carbon σ bond is widely used in complex molecules.

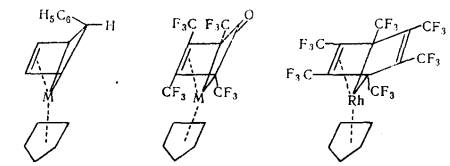
Within the last two years a series of crystallographic investigations made in England by Churchill and coworkers have been published, and these have changed some former concepts about the structure of several complexes and the nature of the bonds.

As long ago as 1959, Wilkinson[130] proposed three possible structures, (XXI), (XXII), and (XXIII), for compounds of the general formula $C_5H_5MC_5H_6$:



The NMR spectra, which are consistent with structure (XXIII), do not, however, agree with the infrared results, and it was impossible to settle the question in favour of one of these structures. A structure analogous to (XXIII) was

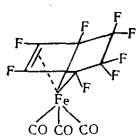
also proposed for the tetrakis(trifluoromethyl)(cyclopentadienone)tricarbonyliron [131]. The proximity of H_α to the central atom and the interaction with non-bonding electrons of the metal explained its mobility and spectroscopic characteristics. The absence of the characteristic H_α bands from complexes substituted in the methylene group is considered a sign that the H_α and not the H_β is substituted and that the substituent is therefore in the *endo*-position [132,133]. However, as an X-ray study of cyclopentadienyl(phenylcyclopentadiene)cobalt has shown [134-136], in fact addition occurs to the cyclopentadiene ring of type (XXIII), but the CHC_6H_5 group departs from the plane of the remaining part of the ring to the side opposite from the metal and the phenyl occupies the *exo*-position (XXIV):



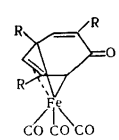
(XXIV) M = Co
(XXVII) M = Rh

(XXV) M = Co
(XXVI) M = Rh

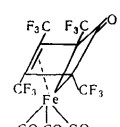
(XXVIII)



(XXIX)



(XXX)
R = H, C_6H_5

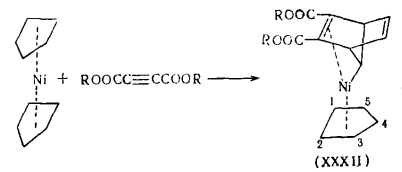


(XXXI)

A quasi-Diels–Alder addition of metal to a diene system, and consequently the rehybridisation of the carbon atoms of the ring which take part in the σ bonding, is shown by X-ray diffraction also for (XXV) [135,137], (XXVI) [138,139], (XXVII) [140], (XXVIII) [138,139,141], (XXIX) [142], (XXX) [143], (XXXI) [144]. The bond lengths, ring conformations, and bond angles show that the bond of the metal with the diene moiety in these molecules consists of one μ and two σ bonds. (XXVIII) is the first example of a localised addition of a transition metal to the benzene ring, as a result of which the planarity and the aromaticity of the ring are completely destroyed. It is thought [142] that the structure of butadienetricarbonyliron, which according to the most recent information [145] contains a delocalised system, should be studied more thoroughly.

Both the metal ion and the other ligands bonded with it play a part in determining the degree of σ bonding. The formation of a localised bond also depends on the fall in the delocalisation energy under the influence of electronegative substituents, such as the CF_3 group. Bailly and coworkers [144] think that the departure from planarity should be taken as a measure of the σ bonding rather than the bond lengths, the difference in which is generally not significant. The greater departure of the ketone group in cyclopentadiene complexes shows the greater $sp^2 \rightarrow sp^3$ rehybridisation of neighbouring carbon atoms. According to Dahl and Smith's results [146] cyclopentadienyl(tetramethylcyclopentadienone)cobalt has, unlike (XXV), a levelled system [sic]§ and as it were a sandwich type of bond. However, the insignificant departure of the carbonyl group which is observed can also be considered as an indication of some localisation of the bond. The localisation energies at appropriate carbon atoms have been calculated [144].

The examples mentioned above showed the possibility of the localised addition of metal to a diene system. The possibility of a greater or less distortion of the delocalisation in a cyclopentadienyl ligand is also not excluded. Dahl and Chin Hsuan Wei [147] first drew attention to this, by studying the structure of the product of the addition of an ester of acetylenedicarboxylic acid to nickelocene (XXXII) [148]:



(XXXII)

The Ni–C and C–C distances in the cyclopentadienyl ring show partial delocalisation in the adduct with a μ bond from $C_{(1)}$–$C_{(2)}$ and a σ bond from $C_{(4)}$. It is thought that this type of bond with cyclopentadienyl is possible in rhodium(I) and nickel(I) complexes. An approximate calculation [149] shows that the structure (XXXIII) is possible for the cyclopentadienyl ring, where the bond order in the $C_{(1)}C_{(2)}C_{(3)}$ group of atoms is relatively lower than in the $C_{(4)}C_{(5)}$ group which is confirmed crystallographically for several complexes which do not possess cylindrical symmetry. The $C_{(1)}C_{(2)}C_{(3)}$ group is always in the *trans*-position to the ligand with the stronger field.

(XXXIII)

Despite the distortion of the delocalisation in the cyclopentadienyl ligand its aromatic nature is evidently unchanged, as in the NMR spectra there is, as before, a single signal for the ring protons [147,148]. This is explained by the dynamic effect of internal rotation.

2. Group VII. Manganese, Rhenium

See Cotton [16] for the early attempts to obtain organic derivatives of manganese and rhenium. Subsequently, iodo(methyl)manganese, dimethylmanganese, and diphenylmanganese, which are unstable to oxidation and insoluble in ether, were obtained [150,151]. With an excess of organolithium reagent they form colourless amorphous insoluble salts of composition $LiMnR_3$. The salts also decompose in air but more slowly than the initial dialkyl derivatives [150]. Dicyclopentadienylmanganese [152] and bis(methylcyclopentadienyl)manganese [153] have been obtained, and their properties show the ionic nature of the bonds in the molecules. These compounds have low oxidation resistance, the first of them burning in air with an explosion. Water and acids immediately destroy it with liberation of cyclopentadiene.

Complexes of the type $MR(CO)_5$, where R represents alkyl, aryl, the corresponding acyl, or fluorinated analogues, are more characteristic derivatives for manganese and rhenium. They are obtained by Method H [20,64,95,154-158] (p. 178), and dinuclear complexes $(CO)_5Mn(CH_2)_nMn(CO)_5$ are obtained by the same method. Features of the structure of some of them are discussed by King [64]. The methyl

§ There is delocalisation of the four π electrons of the tetramethylcyclopentadienone and the CO is tipped out of the plane of the other atoms by 9° away from cobalt (Ed. of Translation).

derivative is also obtained by Method E [159] (p. 173). Some derivatives with an unsaturated σ ligand are obtained by Method F [95] (p. 173), in which, just like the hydrocarbonyls, already prepared $MnR(CO)_5$ can be attached to the diene, to form new derivatives [160]. As for cobalt, here transitions of the σ allyl → π allyl type are characteristic [20,95], and others, but the σ derivatives of manganese are much more stable thermally, and can be isolated and characterised.

The acylcarbonyls of manganese and rhenium are, from their ability to reversible decarbonylation, analogues of the acyl derivatives of carbonylcobalt, although here also great stability is noted. See elsewhere [90,161-163] for the mechanism and kinetics of these changes.

As was recently reported [164], the cations of the carbonyl complexes of manganese and rhenium in alcoholic alkali undergo an interesting transformation into neutral σ carboalkoxycarbonyl complexes:

$$[Mn(CO)_4L_2]^+ + RO^- \underset{HCl}{\rightleftharpoons} ROOC{-}Mn(CO)_3L_2,$$

where L = phosphine, etc.

In this the carbonyl group of the complex is converted into σ bound carbonyl. The reaction is reversible: acid splits off the ester group and the original cation returns.

The preparation of some σ derivatives of dicyclopentadienylrhenium, formed as a result of the addition of dicyclopentadienyl hydride to substituted alkynes, has been described [165].

Perfluoro-alkyl or -aryl and perfluoroacyl derivatives of the carbonyls of manganese and rhenium have been obtained by Methods H [20,64,76,77,107,154] and D [78] (pp. 178 and 173). Perfluoroalkyl derivatives can also be obtained by decarbonylation of perfluoroacyls above 80° for manganese and above 120° for rhenium [20,64,107,154], or by the addition of $MnR(CO)_5$ to fluoroethylenes [75,166-168]. The addition to non-symmetrical fluoroethylenes of the type $CF_2{=}CFCl$ and $CF_2{=}CCl_2$ depends on the reaction conditions. Usually the more fluorinated end of the molecule adds on to the metal, but with ultraviolet irradiation a mixture of products in which the $-CFCl-Mn$ derivative predominates is obtained [167,168]. The irradiation facilitates the addition of methyl- and phenyl-carbonylmanganese to fluoroethylenes.

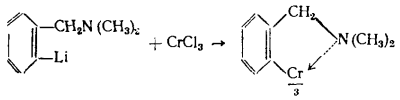
Table 4 contains examples of all classes of the σ derivatives of manganese and rhenium.

3. Group VI. Chromium, Molybdenum, Tungsten

We will not dwell on the well-known history of the phenyl derivatives of chromium, but note only that certain covalent derivatives, stabilised by the addition of solvent molecules — Lewis bases, or carbanions — were isolated in a pure state. First of all, there is $Cr(C_6H_5)_3.3THF$, a red crystalline substance which decomposes at 85° and the product of the addition to it of magnesium salts $Cr(C_6H_5)_3.3THF.3(MgBrCl.THF)$ [169]. In solutions they exist briefly, regrouping into π complexes, and are instantly decomposed by water and mercury(II) chloride. The stabilising action of the tetrahydrofuran molecule is clearly demonstrated by the decomposition of the complex on drying.

The phenylation of chromium(III) chloride with an excess of phenyllithium in ether leads to the formation of $Li_3[Cr(C_6H_5)_6].2\frac{1}{2}$(ether) [170], which later results [171] suggest should be $Li_3[Cr(C_6H_5)_6].4$(ether). It consists of orange-yellow crystals, sensitive to oxygen and atmospheric moisture, capable of being reduced to the monohydride. Corresponding salts of substituted phenylchromium [172] and phenyltungsten [173] have been obtained.

There is proof of the formation of benzyl derivatives of chromium: $[Cr(C_6H_5CH_2)(H_2O)_5]^{2+}$, [174] $[Cr(C_6H_5CH_2)_3]$, and $CrCl(C_6H_5CH_2)_2$, [171] which contain solvent molecules, etc. (XXXIV) has been briefly described — an amino-σ-aryl chelate complex, obtained [175] thus:



(XXXIV)

— as have the alkynyl derivatives $K_3[Cr(C{\equiv}CR)_3(CO)_3]$ [176]. We will not dwell on the role of this kind of chromium derivative in catalytic processes.

By the reaction of molybdenum(V) chloride with an excess of cyclopentadienylsodium, Fischer and Hristidu [177] obtained tetrakiscyclopentadienylmolybdenum. This diamagnetic substance, which is extremely sensitive to oxygen, has one π and three σ cyclopentadienyl groups, according to the authors' results.

General methods for obtaining cyclopentadienylcarbonyl σ complexes (Methods C, D, and E, p. 173) [61] are applicable to various extents to the Group VI metals. Table 5 shows derivatives obtained in this way and some of their fluorinated analogues [69,178]. Among them, the instability of molybdenum compounds of type $Mo(RCO)(C_5H_5)(CO)_3$ has been repeatedly noted. Attempts to obtain them often end in the formation of a dimer cyclopentadienyltricarbonylmolybdenum. Even their perfluorinated analogues are 50–80% decarbonylated during isolation. Unlike them, the analogous acyl complexes of tungsten are completely stable and are not decarbonylated even on irradiation.

The σ allyl derivatives of molybdenum and tungsten, like the iron analogues, are only converted into π allyl complexes on irradiation [179,180].

The interesting thermal decomposition of ethylcyclopentadienyltricarbonylmolybdenum has been described, in which such products as $[Mo(C_2H_5C_5H_4)(CO)_3]_2$ and $(C_5H_5)Mo(CO)_3Mo(CO)_3(C_5H_4C_2H_5)$ are obtained, that is, the ethyl group is transferred from the metal to the ring [181]. This is explained by the general nature of the ethyl–molybdenum bond.

4. Group V. Vanadium, Niobium, Tantalum

According to the results of Meijer and coworkers [182], dicyclopentadienylvanadium is capable of adding alkyl halides according to the equation:

$$2V(C_5H_5)_2 + RX \rightarrow VR(C_5H_5)_2 + VX(C_5H_5)_2.$$

Dicyclopentadienylvanadium dichloride and LiR also give alkyldicyclopentadienvylvanadium. In this way derivatives stable when solid were obtained, with $R = C_6H_5CH_2$ (m.p. 109°), CH_3 (decomp. 80–100°), and C_2H_5, still less stable.

Quite recently, Juvinall [183] reported the production of the first alkyl derivatives of niobium and tantalum by the alkylation of the halides with diethylzinc:

$$2NbCl_5 + 3Zn(CH_3)_2 \rightarrow 2NbCl_2(CH_3)_3 + 3ZnCl_2.$$

TABLE 4. σ derivatives of manganese and rhenium.

Derivative	Colour	M.p., °C	Reference			
			preparation	infrared spectra	NMR	dipole moment
CH_3MnI	red-brown	liquid	150	—	—	—
$(CH_3)_2Mn$	pale yellow	cryst.	150, 151	—	—	—
$[(CH_3)_3Mn]Li$	white	cryst.	150, 151	—	—	—
$(C_6H_5)_2Mn$	green	cryst.	151	—	—	—
$(C_5H_5)_2Mn$	amber	172—173	152	152	152	152
$CH_3Mn(CO)_5$	white	94.5—95	155, 159	108, 154, 155	—	154
$C_6H_5Mn(CO)_5$	»	54	155	154	—	154
$C_6H_5CH_2Mn(CO)_5$	pale yellow	37.5—38.5	155	154, 155	—	154
$CH_2=CH-CH_2Mn(CO)_5$	yellow	b.p. 45°/5 mmHg	95	95	95	—
	white	30	158	—	—	—
$(CH_2)_3[MnCO)_5]_2$	yellow	64—65	64	64	64	—
$C_2H_5OOC-Mn(CO)_3[P(C_6H_5)_3]_2$	»	cryst.	164	164	—	164
$CH_3Mn(CO)_4P(C_6H_5)_3$	pale yellow	110	156, 163	156, 163	—	—
$CH_3COMn(CO)_5$	white	54—55	155	108, 155	—	154
$C_6H_5COMn(CO)_5$	»	95—96	155	155	—	154
	yellow	80.5—81	158	—	—	—
$CH_3COMn(CO)_4NH_2C_6H_5$	»	83—84	161	161	—	—
$CH_3COMn(CO)_4P(C_6H_5)_3$	»	98	163	163	—	—
$CF_3Mn(CO)_5$	white	85	107, 154	107, 108, 154	107	154
$C_2F_5Mn(CO)_5$	»	16	20	20	20, 81	—
$HCF_2CF_2Mn(CO)_5$	pale yellow	30.5—31.5	75, 166	75, 166	75, 166	—
$Cl(CF_2)_4Mn(CO)_5$	ditto	b.p. 58/1 mmHg	107	107	—	—
$CHCl_2CF_2Mn(CO)_5$	»	69	166	166	166	—
$(CF_2)_3[Mn(CO)_5]_2$	white	161	64	64	64	—
$C_6F_5Mn(CO)_5$	»	121—122	77, 78	77	77, 78	—
$CF_3CF=CFMn(CO)_5$	»	76—76.5	20, 76, 107	76, 107	76, 107	—
$CF_3COMn(CO)_5$	orange-yellow	57	107, 154	107, 108, 154	—	154
$CF_3COMn(CO)_4P(C_6H_{11})_3$	lemon-yellow	98	156	156	—	—
$(CF_2)_3(CO)_2[Mn(CO)_5]_2$	pale yellow	105—106	64	64	64	—
$CH_3Re(CO)_5$	white	120	157	154	—	—
$C_6H_5Re(CO)_5$	»	46—47	157	154	—	154
$C_6H_5CH_2Re(CO)_5$	yellow	33—34	154	154	—	—
$CH_3OOCCH=CH-Re(C_5H_5)_2$	orange-brown	161—162	165	165	165	—
$CH_3CORe(CO)_5$	pale yellow	80—81	157	154	—	154
$C_6H_5CORe(CO)_5$	yellow	120 (decomp.)	157	154	—	154
$C_2F_5Re(CO)_5$	pale yellow	39—40	20	20	81	—
$C_2F_5CORe(CO)_5$	ditto	81—83	20	20	81	—
$n\text{-}C_3F_7CORe(CO)_5$	»	54	20	20	81	—

The reaction proceeds in pentane at -78°. The yellow, crystalline, trialkyl derivatives are monomers (from mass spectroscopic studies), volatile, decompose in a few hours at room temperature, but are fairly stable at -78° in the absence of water and oxygen. The tantalum analogue is less thermally stable. Their compositions were determined from the ratio of the products of alkaline hydrolysis.

Somewhat earlier, Fischer and coworkers [184] obtained complexes of composition $M(C_5H_5)_4$ by reaction of tantalum and niobium pentachlorides with cyclopentadienylsodium. These are extremely sensitive to oxygen, monomeric, and paramagnetic. From the infrared analysis, X-ray powder diagrams, and behaviour on hydrogenation, structures with two π and two σ-C_5H_5 groups are proposed.

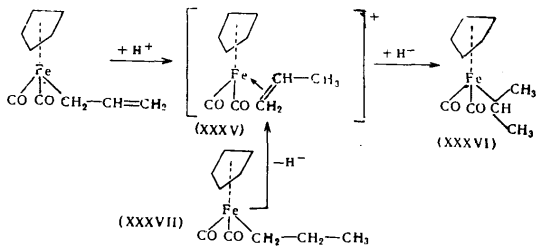
5. σ-Derivative → π-Complex Transitions and the Reverse

In conclusion we think it necessary to mention the interesting reaction, σ-derivative → π-complex and the reverse, which became known from the work of Green and Nagy. They showed that σ allyldicarbonyliron-

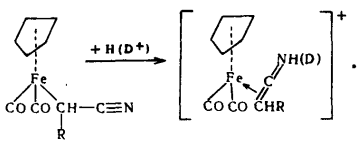
TABLE 5. σ derivatives of chromium, molybdenum, and tungsten.

Derivative	Colour	M.p., °C	Reference		
			preparation	infrared spectra	NMR
$CH_3Cr(CO)_3C_5H_5$	yellow	cryst.	61	61	61
$CH_3Cr(NO)_3C_5H_5$	dark green	82.8—83.2	61	61	61
σ-$C_6H_5Cr(NO)_2C_5H_5$	cinnamon brown	66.5—67.2	61	61	61
$C_6H_5Cr(NO)_2C_5H_5$	green	liquid	61	61	61
$CH_3Mo(CO)_3C_5H_5$	yellow	124 (decomp.)	61	61	61
$C_2H_5Mo(CO)_3C_5H_5$	»	77.5—78.5	61,180	61,180	61
iso-$C_3H_7Mo(CO)_3C_5H_5$	»	29—30	61	61	61
CH_2=CH—$CH_2Mo(CO)_3C_5H_5$	pale yellow	—5	180	180	180
$C_2H_5COMo(CO)_3C_5H_5$	red	liquid	67	67	67
$CF_3Mo(CO)_3C_5H_5$	yellow	153	69	69	69
$(CF_2)_3[Mo(CO)_3C_5H_5]_2$	»	200 (decomp.)	69	69	69
$HCF_2CF_2Mo(CO)_3C_5H_5$	»	53—54	75,178	178	178
$CF_3COMo(CO)_3C_5H_5$	»	64—65	69	69	69
$CH_3W(CO)_3C_5H_5$	red-orange	144.7—145.3	61,62	61	61
CH_2=CH—$CH_2W(CO)_3C_5H_5$	pale yellow	24—26	179	179	179
iso-$C_3H_7W(CO)_3C_5H_5$	dark yellow	b.p. $40/10^{-3}$	179	179	179
$C_2H_5COW(CO)_3C_5H_5$	orange	5	67	67	67
CH_2=CHCOW $(CO)_3C_5H_5$	yellow	57—59	69	69	69
$CHF_2CF_2W(CO)_3C_5H_5$	»	65—65.5 (decomp.)	178	178	178
$CF_3COW(CO)_3C_5H_5$	»	80—82	69	69	69
$C_6F_7COW(CO)_3C_5H_5$	»	53—55	69	69	69

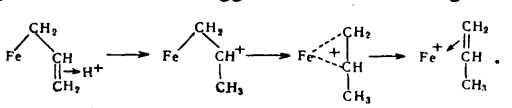
cyclopentadienyl is very easily protonated by gaseous HCl, giving the π propene complex cation (XXXV)[68,185,186]:



The protonation of σ-cyclopentadiene[187], σ-propargyl[188], and σ-cyanoalkyl[189,190] complexes of iron and the σ-allylcyclopentadienyltricarbonyl complexes of molybdenum[180] and tungsten[179] was then studied and it was shown that the reaction is general and always leads to a π-alkene complex cation. Although its products with the propargyl and cyanoalkyl complexes are more complicated there are results which confirm the allene and ketimine structure in the cations obtained:



Results with deuterium chloride show that the third carbon (or hetero-) atom of the ligand its protonated. The following mechanism was suggested for this change:



The reduction of the cations by the hydride reductants leads to neutral σ-alkyl complexes of iso-structure[191]. It was shown that the change (XXXV) → (XXXVI) does not exclude a hydro-complex stage with participation of the Fe–H bond.

The same authors[186,191,192] established the possibility of the change (XXXVII) → (XXXV) as a result of the detachment of the hydride ion from the σ-complex with salts of the triphenylmethyl cation. The change from n-propyl to isopropyl was brought about in this way. The mechanism of the hydride detachment is analogous to that of protonation. The structure of the cation obtained as a result of the hydride ion removal from $Fe(C_5H_5)CD(CH_3)_2(CO)_2$ shows that this occurs at the β carbon atom. In agreement with this is the fact that reaction does not occur with the methyl complex where there is no β carbon, or with the 2-cyanoethyl and 1,1,2,2-tetrafluoroethyl complexes, where such removal is hindered by the neighbouring electronegative groups. The detachment of the hydride ion from the σ ligand is evidently also general, like protonation. For example, it was observed[186] with ethylpentacarbonylmanganese, that is, it is present not only in cyclopentadienyl complexes. These reactions are considered to be models for understanding the mechanism of isomerisation of alkenes in chemisorption.

The following fundamental conclusions can be drawn on the basis of the experimental material considered: (1) comparatively stable carbon–transition metal covalent bonds are formed only in mixed complexes; (2) the observation of Sidgwick's rule in this is not obligatory. There are many examples of stable MR_2L_2 in Group VIII in which the metal is short of two to four electrons for the completed electronic configuration and on the other hand the extremely labile $CoR(CO)_4$ or $NiR(C_5H_5)(CO)$, etc., where this condition is observed, confirm this. These examples of planar complexes show what an important role the steric factors and the nature of the stabilising ligands play; (3) although fluorinated analogues have not yet been obtained for every σ-alkyl (aryl) derivative and the comparison of their stability is purely qualitative it

can be stated, however, that such thermal stability is less probable for σ carbon derivatives, than for σ fluorocarbons. Thus, $Co(CH_3)(CO)_4$ exists only at temperatures below 0° and $CF_3Co(CO)_4$ distils without decomposition at 91°; $Fe(C_2F_5)_2(CO)_4$ decomposes at ~ 100°; whereas $FeR_2(CO)_4$ could not be isolated; $Ti(C_5H_5)_2(C_6H_5)_2$ is stable in a vacuum up to 110° and decomposes at 150°, but $Ti(C_5H_5)_2 \cdot (C_6H_5)_2$ slowly decomposes at room temperature and rapidly at 100°. It must be mentioned, however, that in comparing the thermal stability it is thought that the decomposition mechanisms for the two classes of complexes are the same, although as far as we know there has not been any systematic investigation of the thermal dissociation of either class. Furthermore, in several instances there is no such sharp difference between the fluorinated and unfluorinated analogues.

Hence the factors which determine the stability of a σ derivative can be summarised as follows: (1) the valency state of the metal; (2) the nature of the ligands; (3) the electronegativity of the metal–ligand system (4) the electronegativity of the σ-bound group; (5) steric factors. Their role has been demonstrated, as far as is possible, by experimental data. The extent of the influence of the various factors cannot always be explained sufficiently satisfactorily and apparently it can be different in each particular instance. It is quite evident, however, that it is always necessary to take into account not any of the factors but all of them together.

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MOLYBDENUM CHALCOGENIDES

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1. INTRODUCTION

The investigation of the chemistry of molybdenum can be said to have begun in the first half of the XIXth century, when Berzelius obtained and described some of the principal compounds of molybdenum. Both the metal itself and various of its compounds find wide and diverse applications in industry and in chemical technology. However, several molybdenum compounds of theoretical and practical importance have been studied far too inadequately. These include the molybdenum chalcogenides, that is, the compounds of molybdenum with sulphur, selenium, and tellurium.

It is well known that the most widely distributed molybdenum-bearing mineral — molybdenite — exhibits specific electrical and photoelectric properties and is a semiconducting material.

The field of use of semiconducting materials requires from them the most diverse properties. Therefore an intensive search for new semiconducting substances with various electrical characteristics is now being carried out. In particular, there is now interest in semiconductors which exhibit high thermoelectric characteristics and are suitable for efficient thermoelectric generation.

Because the higher the junction temperature the higher the efficiency of the thermoelement, there is special interest in those materials which exhibit the thermoelectric effect and retain its positive properties at high temperatures. These are, above all, high-melting-point compounds. It is also known that the best thermoelectric materials were obtained from chalcogenides, or combinations of them, which have as constituents metals of high atomic weight. What has just been said explains the special

interest which has recently developed in the chalcogenides in general and in molybdenum chalcogenides in particular.

The practical importance of these compounds necessitates broadly based theoretical investigations, since to obtain semiconducting substances with reproducible properties it is necessary to know the mechanism of their formation, and also all their physicochemical characteristics. The character of the chemical bond, structure, valency state, distribution of electron density in the bonds, magnetic properties, thermodynamic and kinetic characteristics — these are the main directions for the theoretical investigation of thermoelectric materials, including the molybdenum chalcogenides.

A marked intensification of the work on the physicochemical investigation of molybdenum chalcogenides in recent years has led to the production of a series of new facts, which cardinally correct and supplement the old work, the results of which were inadequate, and frequently also erroneous.

In the well-known monographs and reviews[1-4] devoted to the chemistry and technology of molybdenum and its compounds, the information about the molybdenum chalcogenides is usually limited only to their mention and to some of the most general information, mostly out of date.

The authors hope that this review devoted to the chemistry of the molybdenum chalcogenides will make good these deficiencies and allow the reader to obtain exhaustive information, based on the most recent data, about this extremely interesting and promising class of compounds.

On the basis of an analysis of the known experimental data the authors have considered the methods of investigating the molybdenum chalcogenides and of determining the most promising and important regions (in theory and practice) of study of these compounds.

Table 1 gives the chalcogenides of the chromium subgroup elements that are known at present.

Berzelius[21,22] was the first to describe the method of production and some of the properties of the molybdenum sulphides.

The most stable of all the molybdenum chalcogenides is the disulphide MoS_2. It is also the most important sulphide of molybdenum from the practical standpoint. It is the main industrial source for the preparation of molybdenum metal and its compounds.

Molybdenum disulphide, whether natural or artificial, is used as a dry lubricant, forms part of anti-friction lacquer coatings, and allows the production of highly efficient lubricant systems capable of operating at high velocities and at elevated temperatures (up to 400°C), which is especially important in contemporary technology[23-30].

TABLE 1. Chalcogenides of the elements of the chromium subgroup[1-20].

Chalcogen	Metal			
	Cr	Mo	W	U
S	CrS, Cr_7C_8, Cr_5S_6, Cr_3S_4, Cr_2S_3	Mo_2S_3, MoS_2, Mo_2S_5, MoS_3, (MoS_4)	WS_2, WS_3	U_4S_9, US, U_2S_5, U_3S_5, US_2, US_3
Se	$CrSe$, Cr_7Se_8, Cr_5Se_6, Cr_3Se_4, Cr_2Se_3	Mo_2Se_3, $MoSe_2$, Mo_2Se_5, $MoSe_3$	WSe_2, WSe_3	USe, U_3Se_4, U_2Se_5, U_2Se_3, USe_2, USe_3,
Te	$CrTe$, Cr_7Te_8, Cr_5Te_6, Cr_3Te_4, Cr_2Te_3	Mo_2Te_3, $MoTe_2$	WTe_2	UTe, U_2Te_4, U_2Te_5, UTe_2

After molybdenum disulphide, the compound which is second in practical importance and the extent to which it has been studied must be the trisulphide MoS_3, which is widely employed in analytical chemistry[31].

The molybdenum atom has incomplete inner electron shells, which can bring about catalytic activity. The ease of transfer from one valency state to another allows molybdenum to function either as a donor or as an acceptor of electrons. Therefore many molybdenum compounds are used as catalysts for various chemical processes. An important point is that molybdenum compounds exhibit high catalytic activity and selectivity, and are also stable against such a common catalyst poison as sulphur. For example, molybdenum sulphides are used as catalysts in condensations, dehydrations, etc.[32-36].

Of the selenides and tellurides of molybdenum, $MoSe_2$ and $MoTe_2$ have been studied most. The interest in them is due above all to their semiconducting properties.

The following oxide chalcogenides and chalcogenide halides of molybdenum are known: MoO_2S [37], $MoO_2S.3H_2O$, $MoOS_2.3H_2O$ [33], $2MoS_3.MoO_3.9H_2O$, $MoS_3.5MoO_3.6.5H_2O$ [39], $MoCl_2S$ [40], $Mo_5Cl_9S_8$ [41].

2. LOWER CHALCOGENIDES OF MOLYBDENUM

Of the lower molybdenum chalcogenides, the compounds corresponding to the sesqui-composition, Mo_2X_3, are known for all chalcogens.

The first information about the preparation and some properties of molybdenum sesquisulphide was published around 1900, when Guichard[42-44] isolated long steel-grey needles of Mo_2S_3 by brief heating of MoS_2 out of contact with air, at a high temperature. The reaction products were treated with a cold dilute mixture of nitric and hydrochloric acids.

Later Muthmann and Mai[45] obtained well-formed blue-black crystals of Mo_2S_3 on heating MoS_2 (previously boiled in hydrochloric acid) with a mixture of calcium oxide and calcium fluoride. The Mo_2S_3 crystals were separated from the sinter by treating it with concentrated hydrochloric acid followed by elutriation of the unreacted material.

Of the early works it is also worth remembering a low-temperature method of obtaining Mo_2S_3, based on the prolonged action of hydrogen sulphide on a sulphuric acid solution of Mo^{III}, leading to the formation of a black precipitate, which is evidently a hydrated form of molybdenum(III) sulphide[46].

The most contradictory opinions were held for a long time about the formation of molybdenum sesquisulphide from MoS_2 during its thermal decomposition. Thus Guichard[43,44], and later Parravano and Malquori[47], considered that the reduction of molybdenum disulphide in hydrogen proceeds to the metal without formation of intermediate compounds:

$$MoS_2 + 2H_2 = Mo + 2H_2S.$$

It has been reported[48-50] that the thermal dissociation of MoS_2 in a vacuum is also not accompanied by the formation of Mo_2S_3.

In view of the contradictory opinions and the absence of sufficient experimental data, the problem of the existence of Mo_2S_3 and the temperature range of its stability remained unsolved for a long time. A definitive solution of the problem became possible only recently after new precise data about the thermal decomposition of MoS_2 had been obtained, tensimetric investigations had been made, and some physicochemical properties of Mo_2S_3 had been studied.

It is now established that the thermal decomposition of MoS_2, whether in an inert atmosphere, in hydrogen, or in a vacuum, is accompanied by the formation of Mo_2S_3 as an intermediate; its existence has been shown chemically and by X-ray diffraction.

Zelikman and Belyaevskaya [51] showed that in argon MoS_2 rapidly decomposes at 1650–1700°C with formation of a lower sulphide.

The vapour pressure of sulphur over Mo_2S_3 in equilibrium with molybdenum has been measured [52] by the Knudsen method between 1025° and 1150°C and it has been found that not MoS_2 but Mo_2S_3 is in equilibrium with metallic molybdenum and sulphur vapour at these temperatures.

Stubbles and Richardson [53] have shown the error in earlier data [47] on the reduction of MoS_2 in hydrogen at high temperatures. They studied [53] the equilibrium in the Mo–S–H system between gaseous (H_2–H_2S) and solid (Mo–Mo_2S_3 and Mo_2S_3–MoS_2) mixtures at temperatures from 850° to 1200°C by the circulation method. The equilibria are described by the following equations:

$$^2/_3\,Mo + H_2S \rightleftarrows {}^1/_3\,Mo_2S_3 + H_2,$$
$$Mo_2S_3 + H_2S \rightleftarrows 2\,MoS_2 + H_2,$$

which show that the reaction of MoS_2 with hydrogen at high temperatures is accompanied by the formation of Mo_2S_3 as an intermediate. The method of studying the equilibria involves establishing equilibrium between the gases and heated solids on circulating hydrogen over the ground materials [54,55]. The constancy of the hydrogen sulphide pressure was determined by radiochemical determination of its concentration in the gas phase (radioactive sulphur was introduced during the preparation of the sulphides).

The following free energy equations were proposed [53] for the above equilibria:

$$^2/_3Mo(solid) + H_2S(gas) \rightleftarrows {}^1/_3Mo_2S_3(solid) + H_2(gas),\ t = 850\text{–}1200^\circ,$$
$$\Delta G^\circ = -21\,270 + 6.4T \text{ cal } (\pm 100 \text{ cal}),$$
$$Mo_2S_3(solid) + H_2S(gas) \rightleftarrows 2MoS_2(solid) + H_2(gas),\ t = 1000\text{–}1200^\circ,$$
$$\Delta G^\circ = -21\,610 + 8.23T \text{ cal } (\pm 100 \text{ cal}).$$

The free energy equations for the formation of each sulphide from diatomic sulphur and molybdenum are:

$$^4/_3Mo(solid) + S_2(gas) = {}^2/_3Mo_2S_3(solid),$$
$$\Delta G^\circ = -85\,700 + 36.41T \text{ cal}.$$

$$Mo(solid) + S_2(gas) = MoS_2(solid),$$
$$\Delta G^\circ = -85\,870 + 37.33T \text{ cal}.$$

It has been shown [56] that the vacuum thermal dissociation of molybdenum disulphide at 1280°C leads to the formation of the sesquisulphide.

The thermal dissociation of MoS_2 was brought about [56] by putting a few grammes of it in a thoroughly cleaned and previously outgassed quartz ampoule, which was evacuated to a residual pressure of 1×10^{-5} mmHg, sealed and put in a tube furnace in such a way that the end with the substance was in the furnace while the other end projected outside it and could be cooled. The material was heated to a known temperature and held there for a few hours. A sublimate of sulphur condensed in the cold end.

Heating MoS_2 at 1280–1300°C leads to the formation of steel-grey products with a marked metallic lustre, the composition of which corresponds to the formula $Mo_{1+x}S_2$, where x varies according to the time held at a given temperature. The crystal lattice of the phases of variable composition is based on hexagonal MoS_2 with slight distortion in the c direction.

Mo_2S_3 is formed when MoS_2 is heated for a long time under these conditions.

Gorokh and coworkers [57] synthesised Mo_2S_3 from the elements by direct heating of stoichiometric quantities of molybdenum and sulphur in an evacuated quartz ampoule to 500°C and holding at this temperature for 6 h, after which the temperature was raised to 900°C, held there for 14 h, heated again at 1400°C, and held at that temperature for 15 h.

Mo_2S_3 dissociates into the elements at 1600°C, that is, in an inert atmosphere at normal pressure it undergoes thermal dissociation before fusion [57]. Heating Mo_2S_3 with sulphur again leads to the formation of MoS_2. [43,44]

There is evidence that molybdenum sesquisulphide forms a non-stoichiometric compound of composition $Mo_{2.08}S_3$. [52,58,59]

The lower selenides and tellurides of molybdenum have been studied less than the sulphide.

The selenide Mo_2Se_3 is obtained by fusing a finely ground mixture of MoO_2, K_2CO_3, and Se†. The closed crucible with the mixture is put into a furnace at 800°C, the furnace temperature raised to 1200°C, and the mixture held at that temperature for ~1 h until fusion is complete. The cooled melt is treated with water in an atmosphere of nitrogen, to dissolve the potassium selenide. The residue — a steel-grey powder — is Mo_2Se_3. [60]

The telluride Mo_2Te_3 is obtained during the vacuum distillation of the alloy prepared by heating a mixture of molybdenum and an excess of tellurium in an evacuated sealed quartz ampoule. After the reaction the excess of tellurium is sublimed into the cooled upper end of the ampoule, by heating its lower end with the material for a few days at 815–890°C. [61]

Recent work [62,63] on the investigation of molybdenum chalcogenides showed that the lower selenides and tellurides of molybdenum are compounds of variable composition with narrow homogeneity regions. The authors [62,63] note that in composition the molybdenum lower selenides and tellurides do not correspond precisely with the sesqui--compounds, but correspond better with the formula Mo_3X_4 (where X is Se or Te).

As a result of the thermographic investigations and also the data on the vacuum-thermal decomposition of the dichalcogenides, the following general methods for preparing Mo_3Se_4 and Mo_3Te_4 were proposed: (a) thermal dissociation of the molybdenum dichalcogenides — $MoSe_2$ and $MoTe_2$ — in a vacuum at definite temperature ranges; (b) reaction of stoichiometric amounts of the elements in evacuated quartz ampoules; (c) reaction of metallic

† The mixture is covered with a layer of potassium carbonate.

molybdenum with the corresponding dichalcogenide in evacuated quartz ampoules according to the reaction:

$$Mo + 2\,MoX_2 = Mo_3X_4,$$

where X is selenium or tellurium.

All these reaction lead to temperature intervals which ensure the decomposition of the corresponding dichalcogenides to the lower compounds, that is, for selenides at 1180–1240°C, for tellurides at 770–920°C.

The lower molybdenum chalcogenides show great similarities in physical and chemical properties. They are grey crystalline substances, comparatively resistant to attack by acids. At ordinary temperature Mo_2S_3 does not react with hydrochloric and sulphuric acid, or with a mixture of dilute hydrochloric and nitric acids, but it dissolves readily on heating in nitric acid, with the formation of molybdic and sulphuric acids[42-44,57]. The dissolution is apparently due to the reaction:

$$Mo_2S_3 + 10\,HNO_3 = 2\,H_2MoO_4 + 3\,H_2SO_4 + 10\,NO.$$

The molybdenum lower selenide shows similar behaviour[60].

The molybdenum lower telluride is oxidised by nitric acid to MoO_3 and TeO_2, but boiling sulphuric acid is decomposed with the liberation of SO_2 and formation of a cherry-red product of unknown composition[61].

The behaviour of the lower chalcogenides of molybdenum on heating has been insufficiently studied. Such information as has been published[47-53,57] about the thermal stability of Mo_2S_3 has been given in detail above. The molybdenum lower selenides and tellurides are stable in a vacuum up to 1250° and 950°C respectively, above which they dissociate to the elements[61-63].

According to Wendehorst's results[60] the lower molybdenum selenide does not change composition on heating in a stream of H_2Se. However, this is doubtful in the light of subsequent results from studies of the equilibrium in the Mo–S–H system[53] and the great similarity between the properties of these compounds.

The hardness of Mo_2S_3 is somewhat greater than that of MoS_2, and is five on Mohs' scale; the density, determined pyknometrically, is 5.75 g cm^{-3}.[57] The density of the lower telluride is 7.35 ± 0.01 g cm^{-3} at 15°C.

The magnetic properties are known only for the lower telluride of molybdenum. It is paramagnetic, the magnetic susceptibility being $+(0.185 \pm 0.002) \times 10^{-6}$.[61]

A determination of the crystal structure of Mo_2S_3 by the powder method[53] showed that it is tetragonal with unit cell parameters c = 10.9 Å and c/a = 1.27. However, it was shown later[64] that Mo_2S_3 is monoclinic with parameters a = 8.6335 Å, b = 3.208 Å, c = 6.092 Å, β = 102°43′, Z = 2, space group $P2_1/m$, density calculated from the X-ray measurements 5.806 g cm^{-3}.

In the Mo_2S_3 structure each molybdenum atom is situated at a distance of 2.36 Å from three neighbouring sulphur atoms and at a distance of 2.57 Å from three other sulphur atoms (Fig. 1). The molybdenum atoms in direction b are displaced 0.32 Å relative to one another and form a zig-zag chain with Mo–Mo distance of 2.85 Å.

According to Gorokh and coworkers[57], Mo_2S_3 is orthorhombic with the rhombobipyramidal class of symmetry ($3L^23PC$). The Mo_2S_3 crystals are elongated prisms with a rhomb cross-section and angles of 40° and 140° between the adjacent faces. The Mo_2S_3 crystal lattice is similar to the Sb_2S_3 lattice.

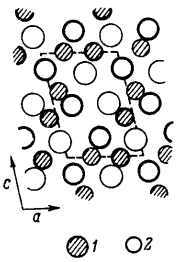


Fig. 1. Structure of Mo_2S_3 projected along axis b. The broken line marks out a unit cell. The atoms at $y = \frac{1}{4}$ are drawn with a light line, those at $y = \frac{3}{4}$ with a heavy line: 1) molybdenum atom; 2) sulphur atom.

TABLE 2. Structural data for Mo_3Se_4 and Mo_3Te_4.

Compound	Symmetry	Lattice parameters, Å			β	Z	Density, g cm^{-3}	
		a	b	c			X-ray	pykno-metric
Mo_3Se_4	monoclinic	4.61	4.77	6.62	93°09′	1	6.88	6.75
Mo_3Te_4	monoclinic	4.87	5.09	7.04	93°46′	1	7.61	7.45

The crystal structure of the molybdenum lower selenides and tellurides has been investigated by the powder method. Mo_3Se_4 and Mo_3Te_4 are isostructural, their crystals are monoclinic. Table 2 gives the results of X-ray investigations[65].

The lower chalcogenides have been studied insufficiently, especially the selenides and tellurides. Probably one of the reasons is that until recently the methods for preparing them were not simple and reliable enough. The methods developed recently for the preparation of molybdenum lower chalcogenides will undoubtedly facilitate their more intensive study[57,62,63].

Structural information about the lower molybdenum chalcogenides is limited to studying them by the powder method. There is a future possibility of obtaining single crystals of these compounds to carry out thorough structural investigations.

Information on the chemical properties of the molybdenum lower chalcogenides is limited to the qualitative characteristics of the behaviour of these compounds in certain acids. It is evident that a study of their reaction with certain elements, with various acids and bases, and also with solid salts and salt solutions, allows interesting data to be obtained on the properties of these compounds, and this in turn opens a path for the preparation of new molybdenum compounds.

3. MOLYBDENUM DICHALCOGENIDES

The molybdenum dichalcogenides are the most stable, most fully studied, and most industrially important compounds of those considered in this review.

The properties of MoS_2 have been described more fully than those of $MoSe_2$ and $MoTe_2$ but the latter are now of special interest in connection with the rapidly developing investigations of semiconductors.

Molybdenum disulphide, molybdenite, is encountered in nature but can be made artificially by various methods. $MoSe_2$ and $MoTe_2$ are only made artificially.

Of the many methods for obtaining molybdenum dichalcogenides we will consider those which are the most general and important in practice (Fig. 2). Several different methods for making MoS_2 have been proposed, but $MoSe_2$ and $MoTe_2$ are made commercially only by the direct reaction of the elements. The exceptional position of MoS_2 is explained above all by the extent to which methods of preparing MoS_2, $MoSe_2$, and $MoTe_2$ have been studied. There is no doubt that further investigation of $MoSe_2$ and $MoTe_2$ will lead to the development of new methods for preparing them, both by methods similar to those for making MoS_2 and by original methods, specific for each of the compounds under consideration.

The method most frequently used for obtaining $MoSe_2$ and $MoTe_2$ — direct synthesis from the elements — apparently still attracts investigators because it allows the purest materials to be obtained, suitable for the investigation of their semiconducting properties without additional purification. However, the use of transport reactions[73,77,82], which not only allow the substances to be purified but also to be obtained in the form of single crystals, make the old preparative methods of interest today.

In addition to the methods for obtaining molybdenum chalcogenides shown in Fig. 2, mention must be made of a method of synthesising crystalline MoS_2, proposed by Spengler[83]. MoS_2 is obtained by the reaction of molybdenum metal or its compounds (molybdenum oxides, salts of molybdic acids, etc.) with sulphur or sulphur(II) compounds (for example, H_2S, alkali metal polysulphides, etc.), in an alkaline medium at 300–500° and at increased pressure in an atmosphere free from oxidising agents.

Methods for obtaining the molybdenum dichalcogenides from the gas phase are also known. Thus MoS_2 can be obtained by the direct reaction of H_2S and CS_2 with molybdenum[84] or by reaction of S and H_2S with volatile molybdenum compounds on heating[85]. The last method can also be used to make $MoSe_2$ and $MoTe_2$.

Of the methods for obtaining molybdenum dichalcogenides which are considered the following are used most often: to prepare MoS_2, the reaction of molybdenum trioxide with sulphur in molten potassium carbonate[70]; to prepare $MoSe_2$ and $MoTe_2$, direct synthesis from the elements[59,73–77].

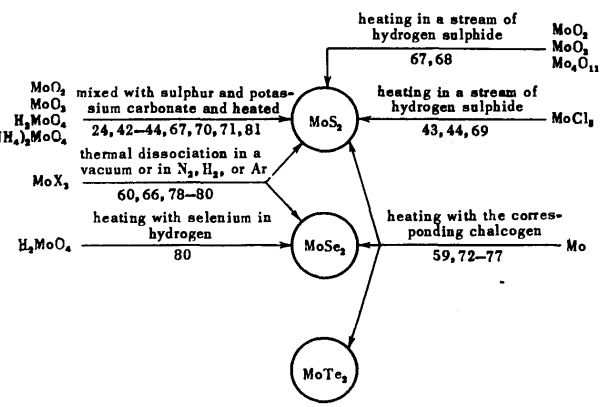


Fig. 2. Methods of preparing the molybdenum chalcogenides (the numbers underneath the arrows are literature references).

In the method of making MoS_2, the potassium carbonate plays a dual role: it serves as a solvent for the sulphur and is a flux, protecting the product formed from oxidation. To obtain MoS_2, four parts by weight of K_2CO_3 are fused with six of sulphur in a closed porcelain retort at 700°. The reaction continues until SO_2 is no longer lost, after which the retort containing the melt is removed from the furnace and cooled. One part by weight of pure MoO_3 (obtained as a sublimate) is added, the retort is heated to 900° and held at that temperature for 30 min. The operation is repeated until six parts by weight of MoO_3 have been added. On cooling, the whole mass solidifies.

The excess of the reagents and the impurities are removed by prolonged boiling in dilute ammonia solution, followed by washing with distilled water, boiling for 30 min in dilute hydrochloric acid, and thoroughly washing with water, alcohol, and ether successively. The product is dired in a vacuum at 75°C.

Bell and Herfert[86] think that the formation of MoS_2 takes place in two stages:

$$2\,MoO_3 + S \rightarrow 2\,MoO_2 + SO_2,$$

$$MoO_2 + 3\,S \rightarrow MoS_2 + SO_2$$

The disulphide obtained always contains MoO_2. These authors were unable to carry out the second reaction to completion by various methods, therefore they removed unreacted MoO_2 present as impurity by treating the material with dilute KCNS (similar to the method developed by Milbauer[87]) with subsequent treatment with dilute solutions of ammonia and hydrochloric acid. This operation almost completely frees the disulphide preparation from MoO_2 and a fairly pure product is obtained ($< 0.01\%$ MoO_2).

It is interesting to note that in the reaction of various molybdenum oxides (for example, MoO_3, MoO_2, Mo_4O_{11}) with hydrogen sulphide at 400–550°C, the final product always contains some MoO_2 as well as MoS_2.[68] The process takes place differently, depending on the initial substance. With molybdenum trioxide the following reactions are possible:

(a) exchange of oxygen with sulphur:

$$MoO_3 + 3\,H_2S \rightarrow MoS_3 + 3\,H_2O;$$

(b) reduction of the higher oxide to MoO_2:

$$MoO_3 + H_2S \rightarrow MoO_2 + H_2O + S;$$

(c) reaction of MoO_2 with hydrogen sulphide:

$$MoO_2 + 2\,H_2S \rightarrow MoS_2 + 2\,H_2O;$$

(d) decomposition of the sulphide obtained earlier (a) at 400–500°C:

$$MoS_3 \rightarrow MoS_2 + S.$$

The reaction of Mo_4O_{11} with hydrogen sulphide proceeds as follows:

$$Mo_4O_{11} + 3\,H_2S \rightarrow 4\,MoO_2 + 3\,H_2O + 3\,S,$$

and subsequently by scheme (c). When the initial substance is MoO_2 the reaction with hydrogen sulphide apparently leads only to reaction (c).

The reaction products always contain MoS_2 and MoO_2, the sum of the stoichiometric coefficients $(x + y)$ in the empirical formula MoO_yS_x are often greater than two, which shows that either elemental sulphur or MoS_3 is present in the products.

As molybdenum disulphide has recently been widely used in technology as a lubricant, the problem arises as to the methods for obtaining pure MoS_2 containing $\gtrsim$ 0.2% impurities. Quartz, 5–7% of which is present in molybdenite concentrates, is an especially harmful impurity. Therefore to obtain pure MoS_2 suitable for use as a lubricant the natural concentrates are subjected to many treatments, which greatly increases the cost of the product[24]. The use of flotation-leaching chemical purification in association with the grinding of molybdenite in ball mills enables a sufficiently pure (99.8%) MoS_2 to be obtained from natural molybdenite concentrates[88].

However, it is more economical to obtain pure MoS_2 by artificial means. A proposed[81] method of preparing MoS_2, by the reaction of MoO_3 or $CaMoO_4$ with sulphur in molten sodium carbonate at 700°C, allows a product with the theoretical ratio of the elements to be obtained.

The direct synthesis of the molybdenum dichalcogenides from the elements is carried out as follows. Stoichiometric amounts of the pure powdered elements are mixed well and put into a quartz ampoule which has previously been cleaned and thoroughly outgassed in a vacuum. The ampoule is outgassed to a residual pressure of 10^{-5} mmHg, sealed, and heat treated, to ensure completion of the reaction and to give a homogeneous product. The ampoule with the reaction mixture is heated slowly in a furnace having smooth temperature regulation. As Table 3 shows, the temperature and holding time in the thermal treatment are different for different authors.

Obviously a higher temperature in the preparation ensures a more rapid completion of the reaction and the best homogenisation of the product. However, in high-temperature preparations explosion of the ampoule is possible. Therefore it is more convenient to carry out direct preparation from the elements at low temperatures, when this is possible, as was suggested for the explosion-free preparation of compounds of the $A^{II}B^{VI}$ type[89].

TABLE 3. Conditions for the preparation of molybdenum dichalcogenides from the elements in evacuated quartz ampoules.

Compound prepared	Heat treatment conditions		Reference
	temp., °C	time, h	
$MoSe_2$	700 anneal I	100	74
$MoSe_2$ / $MoTe_2$	600—700 anneal II	10—15	73
	1000—1200	10—15	76
$MoTe_2$	1100	5—10	75
$MoTe_2$*	460	16	61
$MoTe_2$**	580	20	
	640	24	
	780	48	
	640	40	
	775	24	
$MoTe_2$	600	2 d	77

* After the reaction the product was crushed, passed through a 125 mesh sieve and heated at 600°C for 48 h in a vacuum.

** In preparing $MoTe_2$, an excess of tellurium was taken; after the reaction it was removed by sublimation at 580–815°C in a vacuum.

Finally, in this instance the time of heat treatment to obtain a homogeneous product should be greatly increased.

All the molybdenum dichalcogenides are crystalline. As is known, the ions S^{2-}, Se^{2-}, and Te^{2-} have large radii (1.82, 1.93, and 2.11 Å respectively[90]), and consequently can readily be polarised. On the other hand, the Mo^{4+} ion, which has an ionic radius of 0.65 Å,[90] is a strongly polarising anion. Under such conditions, when the anion is readily polarised and the cation exhibits strong polarising properties, compounds of the type AX_2 show layer structures[91], which have a layer of the cation atoms situated between two layers of anion atoms, as a result of which a packet of three layers is formed. The bonds inside the three layers are considerably stronger than those between two three-layer packets. The molybdenum dichalcogenides are representatives of just this type of layer structure.

Natural molybdenite forms normally flat, thin, very flexible, soft, blue-grey flakes or scales, greasy to the touch and similar to graphite. Its crystals are hexagonal[92,93], space group $P6_3/mmc$–D^4_{6h}. The unit cell contains two MoS_2 molecules and has the following parameters[94]: a_0 = = 3.16 Å, c_0 = 12.32 Å, a_0/c_0 = 1 : 3.899.

Molybdenite has the typical layer structure. The layers of molybdenum ions are situated between two layers of sulphide ions parallel to the $(000\bar{1})$ plane. The ions in the layers are joined by strong bonds and the slip forces between such triple packets are very weak and apparently are of the van-der-Waals type.

This also explains the properties of molybdenite, such as the exceptional ease of slip in the direction perpendicular to the c axis — cleavage is completely by $(000\bar{1})$, the predominant flaky form.

Molybdenum has a coordination number of six in MoS_2 but because of the peculiar electronic structure of molybdenum it corresponds to a trigonal prism and not an octahedron. A molybdenum atom is surrounded by six sulphur atoms at the apices of a regular isosceles trigonal prism (Fig. 3).

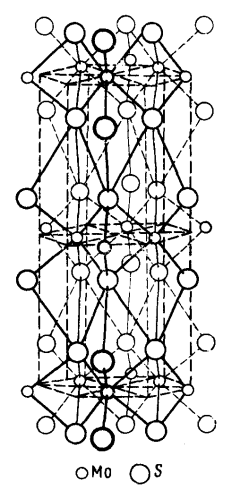


Fig. 3. Structure of hexagonal molybdenum disulphide, MoS_2.

The layer nature of the MoS_2 structure can be represented more graphically[95] as alternating layers of trigonal prisms with Mo^{4+} ions in their centres alternating with empty layers of octahedra (Fig. 4). The hexagonal axis c is perpendicular to the triangular surface of the prism. In MoS_2 the Mo–S distance is 2.35 Å, the S–S distance between two neighbouring layers is 3.66 Å, and the S–S distance in a trigonal prism is much less (2.98 Å)[96].

Synthetic MoS_2, $MoSe_2$, and $MoTe_2$ crystallise as blue-grey tablets or leaflets, and even in thin needles a few millimetres long[70,73,75].

For a long time the crystal structure of MoS_2 remained uncertain, since the preparation of the disulphide was confirmed mainly by chemical analyses, or sometimes microscopically. Although X-ray examination showed the preparation obtained from the elements in an iron tube[72] to have the structure of natural molybdenite, the identity of natural crystals with artificial ones obtained by other methods[67,69,70] was not established. It was suggested that there was a trigonal morphology of artificial MoS_2 crystals[92,97].

The polymorphism of MoS_2 which had been suggested earlier was demonstrated in 1957, when Bell and Herfert[86] obtained the X-ray diagram of synthetic molybdenum disulphide differing in structure from natural molybdenite.

It is now known that MoS_2 can exist in at least two, and possibly in three, polymorphic states[75,86,98–100].

Bell and Herfert[86], who first described a new crystalline form of synthetic MoS_2, obtained by the de Schulten method[70], concluded on the basis of X-ray investigations that the artificial MoS_2, unlike the hexagonal natural molybdenite, is tetragonal with a rhombohedral unit cell, parameters $a = 3.16$ Å, $c = 12.32 \times 1.5$ Å, that is, with the same a parameter, but with the c parameter 1.5 times that for the hexagonal form of the natural disulphide.

The authors[86] explained this difference as follows. Since the interatomic distances in the two modifications are equal, the structures differ in the disposition of the sulphur atoms in the packets, namely: in the hexagonal form a molybdenum atom is situated at the centre of a triangular prism with the three upper sulphur atoms directly above the three lower atoms (Fig. 5a), in the rhombohedral form one layer of sulphur atoms in the packet (for example, the upper) is turned 60° relative to the other (the lower) (Fig. 5b), which on a more thorough examination of the structure leads to octahedral coordination of the molybdenum atom[99].

Hence for the new modification of MoS_2 they proposed a structure with a centre of symmetry, which is described by

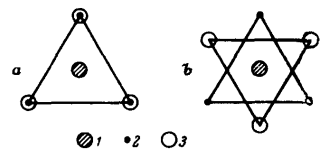


Fig. 5. Coordination of molybdenum atoms in molybdenum disulphide[86]:
a) natural hexagonal MoS_2; b) synthetic rhombohedral MoS_2;
1) molybdenum atom; 2) lower sulphur atoms; 3) upper sulphur atoms.

the space group $R\bar{3}m$–D^5_{3d}, that is, a $CdCl_2$-type structure, where the mutual orientation of the three layers is effected so that only the fourth layer of anions repeats the first, the fifth repeats the second, and so on.

However, this structure did not correspond sufficiently accurately with reality, because of the great discrepancies between the theoretical and experimental intensities of the reflections.

Subsequently a new rhombohedral MoS_2 structure was considered and worked out more precisely. A scheme was proposed[98] with triangular-prismatic coordination of the molybdenum (Fig. 6). The structure shown can be described by space group $R3m$–C^5_{3v} with the following distribution of atoms:

3 molybdenum atoms in 3 (a): 00z with z = 0.000
3 sulphur atoms I in 3 (a): with z = 1/4.001/4
3 sulphur atoms II in 3 (a): with z = 5/12.005/12.

This scheme for the rhombohedral modification of molybdenum disulphide agrees well with the experimental results.

Semiletov[99] confirmed this theoretically. He showed that a structure of the $CdCl_2$ type proposed by Bell and Herfert[86] for rhombohedral MoS_2 was wrong and the constructed a model of a structure with the molybdenum atoms distributed in a trigonal prism (and not in an octahedron, as they should be according to Bell and Herfert).

According to Semiletov[99] the rhombohedral modification is obtained from the hexagonal by rotating through 60° entire three-layer packets and not one of the layers of a single packet, which leads to a structure without a centre of symmetry and with space group $R3m$–C^5_{3v}.

Knop and MacDonald arrived at the same conclusion[75]. They considered both layer structures consisting of hexagonal layers of atoms of molybdenum and sulphur situated

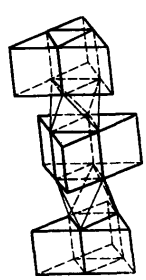


Fig. 4. Structure of MoS_2.[95]

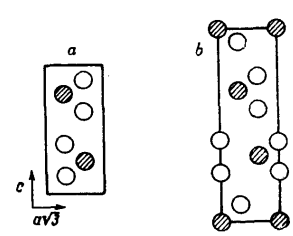


Fig. 6. Polymorphic structure of MoS_2:[98]
a) hexagonal form; b) rhombohedral form.

parallel to the basal plane as differing from one another in the sequence of periods of combination of packets with respect to one another, namely:

. . . AMA BHB/AMA BHB/AMA . . . for the hexagonal form,
. . . APA CMC BHB/APA CMC BHB/APA . . . for the rhombohedral form,

where *A*, *B*, *C* refer to sulphur layers and *M*, *H*, *P* to molybdenum layers. However, in both instances they give trigonal-prismatic coordination of the molybdenum atoms with the nearest atoms of sulphur.

Hence in hexagonal MoS_2 with parameter c = 12.32 Å there are two three-layer packets and in the rhombohedral, the lattice parameter of which is 1.5 times as much (a ratio of 3 : 2), there are three packets.

Apparently the rhombohedral form of MoS_2 is unstable and on prolonged heating it is converted into the stable hexagonal form[79].

Study of the chemical bonds in molybdenite, where the Mo^{IV} atom has a coordination number of six, leads to the conclusion that the six sulphur atoms do not form an octahedron around the molybdenum, but — by virtue of the special structure of the electronic cloud of the molybdenum atom — a triangular prism with a ratio of the axes equal to unity, and S–Mo–S angles of 82° and 136°.[92,101-103]. dsp orbitals participate in the bondformed. Most investigators think that d^4sp hybridisation occurs here, that is, 4*d*, 5*s*, and 5*p* electrons of the central atom participate in the formation of the bond and the only 4*d* orbital (fifth shell) not participating in the bond of the molybdenum atom is occupied by two electrons (one unshared pair)[104-106].

Barinskii and Vainshtein[104] confirmed the d^4sp hybridisation by investigation of the fine structure of X-ray absorption and emission *L* spectra of molybdenum in MoS_2. Knop and MacDonald[75] consider that the magnetic properties of MoS_2 confirm that bond; they think that this results in the diamagnetism and the considerable anisotropy of the diamagnetism of MoS_2 crystals, in which the negative susceptibility in a direction parallel to the hexagonal axis is almost twice that in the direction perpendicular to the axis. The marked temperature dependence of the magnetic properties of molybdenite crystals[107-109] and also the considerable electrical conductivity in the direction perpendicular to the hexagonal axis (that is, along the base of the plane)[110], is explained by the existence of strongly delocalised mobile π-electrons inside the layers, which can be understood, starting from d^4sp orbital configuration of the molybdenum atom.

Investigation of the structure of $MoSe_2$ and $MoTe_2$ began only recently. A hexagonal modification of MoS_2 type is known for these compounds, with space group $P63/mmc$–D^4_{6h}. Table 4 shows some structural characteristics of $MoSe_2$ and $MoTe_2$.

Fig. 7 shows the structure of the ditelluride schematically. The Te–Mo–Te angles[75,76] are respectively α 80.74° ± ± 0.50° and 80.4°; β 83.10° ± 0.60° and 83.5°; γ 134.95° ± ± 0.60° and 133.9°, which corresponds to d^4sp hybridisation[101].

Molybdenum diselenide and ditelluride are thought to be structurally isomorphous with molybdenum disulphide. As MoS_2 exhibits polymorphism, the structural data for $MoSe_2$ and $MoTe_2$ obtained by different methods should be considered incomplete.

TABLE 4. Structural characteristics of molybdenum diselenide and ditelluride.

Compound	Lattice parameter, Å		Density, g cm^{-3}		Interatomic distance Mo–X, Å	Unit cell volume, Å^3	Reference
	a_0	c_0	X-ray	pyk			
$MoSe_2$	3.288	12.900	6.98	6.9		120.8	73
	3.284	12.88	7.0	6.9			74
	3.288	12.931	6.96		2.49		111
	3.289	12.921					118
$MoTe_2$	3.517	13.949	7.8	7.7		149.4	73
	3.518	13.974	7.78	7.68	2.71	149.79	75
	3.519	13.964	7.78	7.8	2.736		76
			7.78	6.85			77
				7.60			61

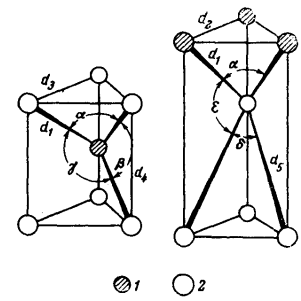


Fig. 7. Coordination of molybdenum and tellurium atoms in molybdenum ditelluride:
1) molybdenum atoms; 2) tellurium atoms.
d_1(Mo–Te) = 2.716 Å;
d_2(Mo–Mo) = d_3(Te–Te) = a_0 = 3.5182 Å;
d_4(Te–Te) = 3.603 Å;
d_5(Te–Te) = 3.945 Å;
d_6(Mo–Mo between layers) = 7.276 Å;
α(Te–Mo–Te) = α(Mo–Te–Mo) = 80.74°;
β(Te–Mo–Te) = 83.10°;
γ(Te–Mo–Te) = 135.95°;
δ(Te–Te–Te) = 52.96°;
ϵ(Mo–Te–Te) = 100.59°.

It is interesting that in the thermal dissociation of molybdenum trisulphide or ammonium thiomolybdate products of composition MoX_{2+x}, or sometimes $Mo_{1-x}S_2$, are obtained under definite conditions[78,79,112]. x decreases as the decomposition temperature is raised. Such products are considered as subtractional solid solutions based on hexagonal MoS_2 with disorder in the crystal lattice: the higher the value of x, the more distorted the structure in the direction of axis c. Above 800° ordering of the structure occurs and stoichiometric molybdenum disulphide is obtained.

The molybdenum dichalcogenides exhibit semiconducting properties. The quality of different thermoelectric materials is compared by use of the figure of merit, which is calculated by the formula[113]:

$$Z=\frac{\alpha^2\sigma}{\kappa},$$

where α is the Seebeck coefficient, σ the electrical conductivity, and κ the thermal conductivity.

At the same time the efficiency of the thermoelectric element increases with the temperature of the hot junction[114].

TABLE 5. Electrical and thermoelectric properties of the molybdenum chalcogenides.

Compound	Electrical conductivity, Ω^{-1} cm^{-1}	Electrical resistivity, Ωcm	Seebeck coefficient, mV deg^{-1}	Thermal conductivity, t*, cm^{-1} deg^{-1}	Figure of merit, deg^{-1}	Type of conductivity	Reference
MoS_2	–	–	72.7 (mean in range 20–80°)	–	–	–	115
	$4.2–9.0 \times 10^{-3}$ (in range 183–500°)	–	–	–	–	p	120
	–	–	–	4.75×10^{-4}	–	–	119
$MoSe_2$	–	3.44×10^3 at 25° 4.76×10^6 at −196°	900	0.023	1.02×10^{-5}	n	73
	1.23×10^{-4} at 22° 2.30×10^{-4} at 62°	–	610–430 (in range 25–150°)	–	–	p	74
	–	20.0 at 100° 1.0 at 600°	−900 at 100° +190 at 600°	–	–	n- at 100° p- at 600°	118
$MoTe_2$	–	8.5×10^3 at 25° 1.34×10^6 at −196°	780	0.020	3.66×10^{-6}	n	73
	–	25.0 at 100° 0.1 at 600°	−360 at 100° −104 at 600°	–	–	–	118

* t is presumably g cal s^{-1} (Ed. of Translation).

Consequently, to obtain large thermoelectric effects, materials with a high Seebeck coefficient and low thermal conductivity, capable of retaining these properties at high temperatures, are required.

Table 5 gives the electrical and thermoelectric characteristics of the molybdenum chalcogenides.

Interesting structural and thermoelectric investigations were made with compositions of the systems $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ and $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$.[116] It was shown that compositions of the first system at $x \leq 0.65$ have a space group of type $CdCl_2$ (D^5_{3d}); after this there is a narrow two-phase region with approximately the same intensity for both types, and with $x > 0.8$ all the compositions crystallise in the space group of MoS_2 type (D^4_{6h}). The pyknometric and X-ray densities of compositions in the system were compared.

A structural study of the $W_xMo_{1-x}Se_2$ system showed a linear dependence of lattice parameters (a, c, c/a, ρ_{X-ray}) on x: with successive replacement of molybdenum by tungsten a decreases c increases (Table 6). All the compositions in this system crystallise with MoS_2-type structures.

The thermoelectric characteristics for the composition of these systems have been given. Since the conductivity mechanism in $MoSe_2$ is electronic (n type), but that in WSe_2 is hole (p type), the solid solutions of these compounds of different conductivity types show high electrical resistivity, due to compensation of two opposing conductivity mechanisms. $TaSe_2$ has a comparatively high electrical conductivity and is a metal-like conductor[73,117]. Brixner and Teufer[116] showed that by varying the concentration of the individual components in the compositions of the $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system, the optimal values of the parameters in which an investigator is interested can be found.

TABLE 6. Lattice parameters of compositions of the $W_xMo_{1-x}Se_2$ system.

Composition	a, Å	c, Å	c/a	ρ_{X-ray}, g cm^{-3}	Unit-cell volume, Å^3
$MoSe_2$	3.289	12.930	3.931	6.959	121.128
$Mo_{0.85}W_{0.15}Se_2$	3.289	12.935	3.933	7.318	121.175
$Mo_{0.75}W_{0.25}Se_2$	3.288	12.941	3.936	7.560	121.157
$Mo_{0.65}W_{0.35}Se_2$	3.288	12.945	3.937	7.799	121.195
$Mo_{0.25}W_{0.75}Se_2$	3.287	12.965	3.944	8.754	121.308
WSe_2	3.286	12.976	3.949	9.353	121.337

Guennoc[77] stated that solid solutions corresponding to the general formula (Mo, W)(Se, Te)$_2$ with additions of niobium or tantalum can operate as thermoelectric materials at 200–400°.

There is great interest in investigating thermoelectric materials in the problem of obtaining substances with thermal conductivities as low as possible. As Ioffe and coworkers showed[121], this can be achieved by fusing the thermoelectric material with an isomorphous element or alloy. Then in the solid solution of two isomorphous crystals the short-range periodicity of the lattice is destroyed, which leads to considerable scattering of phonons. Such destruction of the short-range order of the crystal lattice of the material (while retaining the long-range periodicity) gives a marked decrease in thermal conductivity at very small change in mobility of the charge carriers, which leads to a considerable increase in the figure of merit.

Brixner and Teufer[116] attempted to obtain such alloys based on the $W_xMo_{1-x}Se_2$ system. The results of measuring the thermal conductivity of these compositions show that the thermal conductivity of an alloy of the two isomorphous substances WSe_2 and $MoSe_2$ is less than the thermal conductivity of either of its components and is least when half the tungsten atoms have been replaced by molybdenum.

Study of various alloys of the molybdenum dichalcogenides MoS_2, $MoSe_2$, and $MoTe_2$ with the structurally isomorphous tungsten chalcogenides and also with additions of metals of the neighbouring groups of the Periodic System (for example, niobium, tantalum, rhenium, etc.) for thermoelectric purposes is a future problem of the chemistry of the molybdenum chalcogenides.

The coefficient of thermal conductivity of molybdenite MoS_2 at 80°C is $\kappa = 4.75 \times 10^{-4}$ cal cm^{-1} deg^{-1} s^{-1}.[119] Since the thermal conductivity of semiconductors is of great importance for determining the usefulness and quality of a material, such data are of great interest.

In semiconductors the thermal conductivity is made up of the transfer of heat by waves of thermal motion of the

molecules of the lattice (or phonons) κ_{ph} and from the transfer of the energy of the free charges (or electrons) κ_{el}. However, phononic thermal conductivity plays the principal part, since for semiconducting materials the part of the thermal conductivity which is determined by the diffusion of electrons is negligible.

In semiconductors with carrier current of a single sign the electronic constituent of the thermal conductivity κ_{el} is determined by the Wiedemann–Franz law:

$$\kappa_{el} = \frac{k^2}{e^2} A\sigma T,$$

where k is the Boltzmann constant, e the charge of an electron, A a coefficient (= 2 when undegenerate), σ the electrical conductivity, and T the absolute temperature.

The value $\sigma = 4.3\ \Omega^{-1}\ cm^{-1}$ was found for molybdenite at $T = 353°K$, and the electronic thermal conductivity was calculated to be $\kappa_{el} = 0.0557 \times 10^{-4}$ cal cm^{-1} deg^{-1} s^{-1}.[119] Consequently the phononic thermal conductivity is $\kappa_{ph} = \kappa - \kappa_{el} = 4.75 \times 10^{-4} - 0.0577 \times 10^{-4} = 4.69 \times 10^{-4}$ cal $cm^{-1} \times deg^{-1}\ s^{-1}$, which is ~ 84 times the electronic thermal conductivity. However, it is clearly evident that lattice vibrations make the main contribution to the mechanism of the thermal conductivity of MoS_2.

The Debye temperature for MoS_2 is $\Theta = 209°K$.[119] The dielectric constant of MoS_2 at -196°C is $\epsilon = 7.6$.[122]

The electrical conductivity of molybdenite has been measured over a wide range of temperatures: from 100° to 500°K.[110] It was shown that the electrical conductivity along the basal plane, that is, in the direction perpendicular to the c axis ($\sigma_\perp$), is approximately 10^3 times greater than that in the direction parallel to the hexagonal axis ($\sigma_\parallel$). Ohm's law is obeyed on passing current in the two directions at ~ 420°K, but at room temperature Ohm's law is not obeyed in either direction (Fig. 8).

Measurements of the electrical conductivity in molybdenite crystals at high temperatures show the electronic nature of the conductivity[110]. The mechanism of electronic conductivity in MoS_2 is confirmed by the measurements of the surface conductivity of thin plates of molybdenite cleaved off natural crystals. The surface conductivity rises in an atmosphere of ammonia vapour and falls in an atmosphere of nitric acid vapour. Apparently the adsorption of the vapours of these substances changes the mobility and concentration of the charge carriers[123–125].

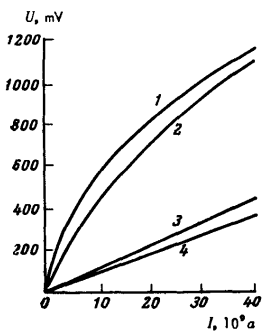


Fig. 8. Dependence of the electrical conductivity of crystals of molybdenite on the stress[110]:
1) $\sigma_\parallel$ at room temperature; 2) $\sigma_\perp$ at room temperature; 3) $\sigma_\perp$ at ~ 420°K; 4) $\sigma_\parallel$ at ~ 420°K.

An investigation of the magnetic properties of MoS_2 confirms the presence of free electrons in the planes of the crystal. Considerable anisotropy (~ 72%) of the diamagnetism of molybdenite crystals was found: the susceptibility in the direction parallel to the hexagonal axis is $\chi_\parallel = -87.1 \times 10^{-6}$, and that in the direction perpendicular to this axis is $\chi_\perp = -44.3 \times 10^{-6}$.[107] Such an increase in diamagnetism in the direction perpendicular to the basal plane is due to the presence of free electrons, which are completely free in the plane of the base but have restricted mobility in the perpendicular direction. A similar diamagnetism of free electrons was found earlier for graphite[126,127].

Still more conclusive facts in support of this were obtained on measuring the magnetic properties of MoS_2 at various temperatures[108,109]. It is known that the susceptibility of free electrons is very sensitive to a change in temperature. With weak magnetic fields and not very low temperatures the diamagnetic susceptibility of the electron gas is[128]:

$$(\chi_e)_{dia} = -\frac{nN\mu_B^2}{3kT},$$

where n is the number of free electrons per unit volume, N Avogadro's number, μ_B the Bohr magneton, k the Boltzmann constant, and T the absolute temperature.

The results of measurements of the temperature dependence of the susceptibility of molybdenite shows that the observed electron susceptibility of MoS_2 equals the diamagnetic susceptibility of free electron gas having an electron density of 0.3 electron per atom[108]. The temperature dependence of the diamagnetic anisotropy resembles the behaviour of graphite single crystals on heating[129].

The above suggests that in MoS_2, where the bond between the molybdenum and sulphur atoms is covalent, bonds of partly metallic character are formed along the basal plane, which agrees well with the results of electric and magnetic measurements of molybdenite crystals. For $MoTe_2$ the specific magnetic susceptibility is -0.345×10^{-6}.[61]

The effect of pressure on the electrical resistivity of MoS_2 has been investigated[130]. At $P = 20$ kbar and 296°K the resistivity of MoS_2 is 300–600 Ω cm. The resistivity decreases considerably with increase in pressure. Phase transformations were not observed up to 500 kbar.[130]

The optical properties of single crystals of MoS_2[131–134] and $MoTe_2$[135] have been studied, using very thin crystals (thickness: MoS_2 100 Å, $MoTe_2$ 200–1000 Å), obtained by splitting at cleavage planes. The optical spectra give valuable information about the bond energies and the excited state in the crystal. Conclusions about the covalent nature of the bonds in crystals of MoS_2 and $MoTe_2$ can be drawn from the spectra.

The molybdenum dichalcogenides are rather stable. For a long time the melting point of molybdenite was thought to be 1185°.[97] Zelikman and Belyaevskaya[51] found, by subjecting MoS_2 to rapid and short-time (2–3 min) heating, that specimens of MoS_2 start to melt at 1650–1700°C; this is accompanied by intensive decomposition with formation of a lower sulphide. However, Cannon[136] considers that this temperature is depressed owing to the reaction of the material with the graphite vessel used in the work[51]. On

heating specimens of MoS_2 in molybdenum crucibles in a vacuum, he[136] observed fusion on heating for 10 min at 1800° ± 20°C. He concluded that if MoS_2 obeys Tammann's rule, that is, the temperature for the start of appreciable sintering is approximately one-half *Tf*, then the melting point of MoS_2 must be ~2375°C.

In view of the contradictory data[51,136], the problem of the melting point of MoS_2 requires further investigation. However, it is clear that the above experimental results[51,136] are erroneous. As shown recently[56], when heated in a vacuum MoS_2 decomposes before melting, and when heated for a sufficient time even at 1280°C the dissociation of MoS_2 is accompanied by the formation of the sesquisulphide. At 1400°C the thermal decomposition of MoS_2 goes to metallic molybdenum[137]. On heating MoS_2 to a temperature above 1000°C, sintering of the material occurs and the surface of the MoS_2 is covered with a dense, difficultly permeable scale, which retards the dissociation[56,138]. This may be the reason for the erroneous results[136].

Careful examination of Zelikman and Belyaevskaya's results[51] suggests that the dissociation of MoS_2 in an inert medium also starts before 1350°C, as is shown by the chemical analysis of the products. Although their X-ray diagrams do not differ from that of the original disulphide it is evident from the chemical analysis that the products of the heating are appreciably enriched in molybdenum. Probably there is formation of a phase of type $Mo_{1+x}S_2$, based on the hexagonal MoS_2 type which has been described[56]. The authors[51] concluded that MoS_2 had no phase transformations up to 1350°C according to the results of the heating curves recorded with a pyrometer; this is evidently due to a very small rate of dissociation of molybdenum disulphide and consequently an insignificant thermal effect.

It must be emphasised that both the formation and the dissociation of the chalcogenides take place rather slowly, especially at low temperatures. This must be remembered in considering various equilibria in chalcogenide systems. This is why the published results[51,136] obtained in short-time heating should be regarded critically.

$MoSe_2$ and $MoTe_2$ dissociate with formation of lower chalcogenides when heated in a vacuum to 1170° and 750°C respectively[61,62].

The thermodynamic characteristics of MoS_2 are known[139-141]. Smith and coworkers[140] carried out calorimetric measurements and calculated some thermodynamic quantities for solid MoS_2 at low temperatures (Table 7).

The free energy and heat of formation of MoS_2 from the elements have been calculated[53]:

$$\Delta G^\circ_{298} = -78\,420 \text{ cal}, \qquad \Delta H^\circ_{298} = -91\,340 \text{ cal}.$$

TABLE 7. Smoothed values of the molar thermodynamic functions for solid MoS_2.

T, °K	C_p, cal × ×mole^{-1}deg^{-1}	S°_T, e.u.	$\frac{-(G^\circ_T-H^\circ_0)}{T}$, cal mole^{-1} × × deg^{-1}	$\frac{(H^\circ_T-H^\circ_0)}{T}$, cal mole^{-1} × × deg^{-1}
20	0.28	0.140	0.055	0.085
30	0.63	0.315	0.110	0.205
40	1.12	0.560	0.190	0.37
50	1.74	0.870	0.290	0.58
60	2.46	1.25	0.420	0.83
70	3.24	1.69	0.570	1.12
80	4.07	2.17	0.740	1.43
90	4.97	2.71	0.930	1.78

The molybdenum dichalcogenides are quite stable in air at room temperature but the finely-divided ditelluride is reported[76] to oxidise slowly.

On heating in air all the compounds burn to form MoO_3 and the corresponding chalcogenide oxide.

Since the oxidation of MoS_2 is widely used industrially for the treatment of molybdenite concentrates the kinetics of the oxidation of molybdenite at 400°, 500°, and 600°C has been studied[142,143]. It is thought[142] that within the range 400–600°C molybdenum disulphide is oxidised by oxygen to MoO_3, without the stage of formation of MoO_2. The mechanism of the oxidation of MoS_2 is probably:

$$MoS_2 + O_{2ads} \rightarrow MoS_2O + O,$$
$$MoS_2 + O_{2ads} \rightarrow MoSO_2 + S,$$
$$MoS_2O + O_{2ads} \rightarrow MoO_3 + 2S,$$
$$MoSO_2 + O_{2ads} \rightarrow MoO_3 + SO.$$

The initial act of reaction of MoS_2 with oxygen consists in the adsorption of oxygen molecules on the surface of the molybdenite. The formation of intermediate compounds of the oxide sulphide type is facilitated by the presence on the surface of the MoS_2, which is a semiconductor, of active centres with free valencies[144]. Above 600°C the secondary reaction of MoS_2 with the MoO_3 occurs, with formation of MoO_2.[142]

Heating in the absence of air gives different results, depending on the conditions of the experiment, which has already been discussed in detail above. As the results of different authors show, the question of the thermal dissociation of molybdenum dichalcogenides under different conditions is still not completely clear. Taking into account that most of these investigations are comparatively old, the problem of the behaviour of the molybdenum chalcogenides on heating remains unsolved and requires repetition of the experiments on a contemporary level.

According to Wendehorst's results[60], when heated in hydrogen, molybdenum diselenide does not give a lower selenide but is slowly reduced to the metal if the temperature is high enough.

Not one of the chalcogenides of the MoX_2 type is converted into a compound richer in chalcogen by heating with the chalcogen concerned[42-44,60,61]. Apparently compounds of the MoX_3 type are always thermodynamically unstable, as Biltz and Köcher[145] found for MoS_3, and the reaction $MoX_3 \rightarrow MoX_2 + X$ must be considered irreversible. However, there have been reports of the possibility of obtaining molybdenum trisulphide by the reaction of the disulphide with elemental sulphur[53].

MoS_2 is rather inert chemically. It is insoluble in boiling water. It reacts with the halogens as follows. On gentle heating, fluorine reacts with crystalline MoS_2 with ignition[42-44]. Below 400°C, chlorine reacts very slowly, forming $MoCl_5$ and the intermediate compounds $MoSCl_2$ and $MoOCl_4$. The chlorination of the disulphide with $Cl_2 + 3O_2$ mixture is thermodynamically more favourable, MoO_2Cl_2 being formed. In the presence of nitrogen oxides or nitric acid fumes the reaction is appreciable even at 170°C.[40] Bromine vapour reacts very slowly; the composition of the reaction products has not been established[146].

When SF_4 is used as a fluorinating agent, molybdenum can be oxidised to the quinquevalent state. Thus the reaction of SF_4 with MoS_2 at 350°C gives MoF_4[147] and with the mixture $2NaF + MoS_2$ at 400° the compound $NaMoF_6$ is formed[148].

$SOCl_2$ does not react with MoS_2 even on heating for a few days[149]. Gaseous hydrogen chloride does not react with MoS_2 at temperatures up to red heat[42-44]. Liquid anhydrous hydrogen fluoride also does not react with the disulphide in the temperature range -18° to -7°C.[150]

However, MoS_2 is completely soluble in *aqua regia*, is decomposed in boiling concentrated sulphuric acid, and is oxidised to MoO_3 in nitric acid.

Aqueous solutions of acids, alkalis, and salts react differently with molybdenum disulphide. Alkali solutions with pH 10 oxidise and dissolve MoS_2 most actively[151]. In acid, neutral, and weakly alkaline solutions the oxidation of MoS_2 is weaker[151]. This is confirmed by an investigation[152] of the anodic dissolution of molybdenite in 0.5–5% solutions of H_2SO_4 and NaOH. The results show that MoS_2 is almost insoluble in these solutions in the absence of current, but is electrochemically soluble. The rate of dissolution increases with increase in current density, increase in NaOH concentration, and decrease in H_2SO_4 concentration. Probably oxidation takes place by the following reactions:

$$MoS_2 + 9O + 3H_2O \rightarrow 2H_2SO_4 + H_2MoO_4,$$

$$MoS_2 + 9O + 6NaOH \rightarrow 6Na^+ + 2SO_4^{2-} + MoO_4^{2-} + 3H_2O.$$

In aqueous solutions of 3 *N* Na_2CO_3 and 8 *N* HCl, MoS_2 is almost insoluble up to 90°C.[153]

The reaction of finely dispersed MoS_2 with water vapour at 200–500°C showed that at 200–300°C a little hydrogen and traces of sulphur dioxide are formed, but at 400–500°C traces of hydrogen and measurable amounts of sulphur dioxide. The gaseous products of the reaction were identified mass-spectroscopically[154].

The reaction of MoS_2 with MoO_3 was studied at 400–700° in an inert atmosphere, in a vacuum, and in SO_2 at atmospheric pressure[155-159]. MoS_2 reacts with MoO_3 to form molybdenum dioxide:

$$MoS_2 + 6MoO_3 \rightarrow 7MoO_2 + 2SO_2.$$

Reaction starts even at 400°C and the reaction rate rises rapidly with the temperature. Below 550°C the reaction products contain (in addition to MoO_2) the intermediate oxide Mo_4O_{11}, which is formed by the reaction:

$$MoS_2 + 12MoO_3 \rightarrow 2Mo_4O_{11} + 5MoO_2 + 2SO_2.$$

This oxide reacts further with the disulphide to form MoO_2:

$$2Mo_4O_{11} + MoS_2 \rightarrow 9MoO_2 + 2SO_2.$$

The results were confirmed by chemical and X-ray analyses.

Solid molybdenum disulphide readily reacts with the alkali and alkaline earth metals dissolved in liquid ammonia[160]. From solutions which contain the alkali metals in excess, black homogeneous compounds of the composition:

$$Cs_{0.5}MoS_2;\ K_{0.6}MoS_2;\ Na_{0.8}(NH_3)_{0.2}MoS_2;\ Li_{1.1}(NH_3)_{0.6}MoS_2,$$

can be separated after filtration, washing with liquid ammonia, and removing the remaining ammonia in a vacuum at room temperature.

The last two compounds do not lose ammonia when held for a long time in a vacuum at room temperature.

All the compounds are extremely sensitive to heat and air. The potassium and caesium compounds glow in air, and react readily with water to form the sulphide and hydrogen, which contains a very slight amount of hydrogen sulphide. On heating in a vacuum a slight amount of alkali metal is detached. At 100°C the preparations decompose appreciably and give new compounds, which correspond to the polarised form of $K^+(MoS_2)^-$ type.

Such compounds are considered as interstitial compounds, in which a layer of alkali or alkaline earth metal is introduced between the molybdenum disulphide layers. The distance between the layers increases considerably with an insignificant increase in the Mo–Mo interatomic distances.

The reaction of liquid ammonia with MoS_2 has been described[161]. Under the influence of the NH_4^+ and NH_2^- ions present in liquid ammonia, at low temperatures there is a disturbance of the layers in molybdenum disulphide, as was shown by recording infrared spectra of thin layers of MoS_2. Adsorption of ammonia leads to far-reaching changes in the mechanical properties of the solid.

The adsorption of argon, krypton, and organic substances on MoS_2 has been studied[162-164].

Carbon dioxide and sulphur dioxide gases do not react with molybdenum disulphide at low temperatures; the reaction only takes place above 500°C and at ~ 800°C there is a sudden increase in the reaction rates. The final product of these reactions is MoO_2.[165]

The main reaction of MoS_2 with carbon dioxide is expressed by the following equation:

$$MoS_2 + 6CO_2 = MoO_2 + 2SO_2 + 6CO.$$

Apart from these products, a little COS, S, and MoO_3 are obtained, due to side reactions taking place.

The reaction of the disulphide with sulphur dioxide follows the equation:

$$MoS_2 + SO_2 = MoO_2 + 3S,$$

which is almost complete at 1100°C.

The molybdenum chalcogenides, like those of other transition metals, are capable of forming ternary phases. Heating MoS_2 with the sulphides of iron group metals at 500–1300°C in an inert atmosphere (argon or nitrogen) or in hydrogen sulphide leads to the formation of a new class of stable crystalline compounds of type $AMoS_y$, where A is the iron-group metal (Fe, Co, Ni) and y = 2.5–3. The $FeMoS_{2.5}$ crystals have strongly expressed ferromagnetic properties[166].

A thermoelectric material of composition Ag_2MoX_3 (where X is selenium or tellurium) is obtained by reaction of the components at 700–1100°C.[167] However, a study of the solubility of copper and silver in molybdenum disulphide by heating the components at 800°C in evacuated ampoules did not give positive results. Compounds similar to Cu_xNbS_2 ($\sim 0.6 \leq x \leq 0.8$) could not be prepared for molybdenum disulphide[168].

In the coprecipitation of thallium with molybdenum trisulphide, the formation of the compound $TlMoS_2$, which is amorphous to X-rays, was established[169,170].

A series of mixed chalcogenides is known for molybdenum[171].

There is only limited information about the chemical behaviour of $MoSe_2$. It is insoluble in hot concentrated hydrochloric acid, but is readily soluble in hot concentrated sulphuric acid with liberation of sulphur dioxide. The

diselenide is completely insoluble in ammonia, and in alkali metal sulphides and selenides, and dissolves very slightly on prolonged boiling in concentrated alkalis[60].

The chemical properties of $MoTe_2$ have been studied even less. Water and hydrochloric and sulphuric acids do not react with $MoTe_2$ on boiling, whereas dilute nitric acid breaks down the ditelluride even in the cold[61].

Finely ground $MoTe_2$ powder is gradually oxidised by atmospheric oxygen at room temperature[76].

4. HIGHER CHALCOGENIDES OF MOLYBDENUM

A. Molybdenum(V) Chalcogenides

Only the sulphide and selenide of molybdenum(V) are known. Mawrow and Nikolow[172] obtained Mo_2S_5 and described its properties. Their method of preparation will now be described.

A solution of 5 g $(NH_4)_2MoO_4$ in 150 ml water was mixed with sufficient concentrated sulphuric acid to give a concentration of 20% H_2SO_4. The acid solution was reduced with metallic zinc to give a dark red coloration, then diluted with an equal quantity of water, filtered, and saturated with hydrogen sulphide. The precipitate which separated was filtered off, washed with hot water until an acid reaction was no longer obtained, and then washed with alcohol. The precipitate was washed to remove free sulphur by repeatedly shaking with carbon disulphide, and was washed on the filter with ether. The moist brown-black precipitate was dried at 68–75°C, whereupon it became dark brown. The compound corresponded to the formula $Mo_2S_5.3H_2O$. Sufficiently pure preparations are obtained when the product is well washed with hot water (to give a negative reaction with H_2SO_4) and carbon disulphide and dried for a long time on a water-bath at 68–75°C in the finely dispersed state.

$Mo_2S_5.3H_2O$ is completely insoluble in water. On boiling with alkalis or ammonia it dissolves with a brown-yellow coloration and liberation of hydrogen sulphide. $Mo_2S_5.3H_2O$ dissolves well in alkali metal sulphides, especially on heating. On cooling, an orange-yellow precipitate separates from the solutions. When heated with concentrated hydrochloric acid the compound dissolves, with a green coloration, but with concentrated sulphuric acid a red-yellow liquid is formed, which gradually turns green with separation of free sulphur and sulphur dioxide.

When heated in air up to 135–140° $Mo_2S_5.3H_2O$ loses one molecule of water and gives the compound $Mo_2S_5.2H_2O$. However, on further heating to 195–200° in air, this compound is partly oxidised.

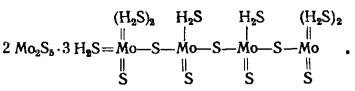
Very careful heating of $Mo_2S_5.3H_2O$ in a stream of carbon dioxide gives brown-black Mo_2S_5. The heating takes place so that the tip of the flame of a burner did not touch the tube which contained the compound.

The sulphide obtained in this way sometimes contains a slight amount of water of hydration, which is very difficult to remove, since at a higher temperature the compound is oxidised and then burns, but heating in a current of hydrogen, even at a very low temperature, leads to partial reduction to MoS_2.

In an attempt to dehydrate $Mo_2S_5.3H_2O$ by heating in a current of hydrogen sulphide the authors[172] obtained a brown-black compound corresponding to the formula $2Mo_2S_5.3H_2S$, which is evidently formed as a result of the replacement of water by hydrogen sulphide by the equation:

$$2(Mo_2S_5 \cdot 3H_2O) + 3H_2S \rightarrow 2Mo_2S_5 \cdot 3H_2S + 6H_2O.$$

The following structural model was proposed for this substance:



The compound is insoluble in water and hydrochloric acid, very difficultly soluble with a green coloration on boiling in sulphuric acid, and on boiling with alkalis and alkali metal sulphides it dissolves to give a yellow solution and separation of a dark green mass, which turns blue in air.

Wendehorst[60] obtained the molybdenum(V) selenide similarly. The precipitate of selenide is decomposed during drying, even in a stream of nitrogen, therefore it is analysed moist. The atomic ratio Mo : Se = 2 : 5 shows that the material obtained is molybdenum(V) selenide.

In its chemical properties the selenide is reminiscent of the corresponding sulphide, but even more unstable. On dissolution in alkalis, sulphides, and acids there is an intense coloration of the solutions.

B. Molybdenum(VI) Chalcogenides

The oldest method for obtaining MoS_3 and $MoSe_3$ consists in the decomposition of solutions of thio- and seleno-molybdates respectively with acids.

Thus Berzelius[21] first obtained a dark brown precipitate of MoS_3 by saturating with hydrogen sulphide a concentrated solution of alkali metal molybdate and then decomposing the thiomolybdic acid which was formed. $MoSe_3$ was obtained similarly[173].

Wendehorst[60] obtained $MoSe_3$ by saturating with hydrogen selenide a solution containing 5 g $(NH_4)_2MoO_4$ in 10 ml conc. sulphuric acid and 50 ml water. The excess of H_2Se was removed with a stream of nitrogen. The black fine-grained precipitate of $MoSe_3$ was washed successively with ice water, alcohol, and ether, and dried in a stream of nitrogen with slow heating.

The MoS_3 and $MoSe_3$ thus obtained always contain an excess of the chalcogen[60,174,175]. To obtain the sulphide in a purer form, an aqueous solution of pure thiomolybdate — for example, ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$ — is first obtained, which is then decomposed by the action of acid (for example, sulphuric acid). A method for obtaining pure solutions of H_2MoS_4 by passing dilute solutions of $(NH_4)_2MoS_4$ through a column with an anion-exchange resin in the H^+ form[176] is interesting.

The so-called "crystalline"‡ molybdenum trisulphide is obtained as fine gleaming black leaflets, resembling graphite, from salts of thiomolybdenic acid with some organic compounds — for example, that with piperazine, $C_4H_{10}N_2.H_2MoS_4$ — by decomposing them with hydrochloric or acetic acid[177].

Molybdenum trisulphide is obtained in the high-temperature reaction of KCNS with MoO_3.[178–181]

‡ Reported[78] to be amorphous to X-rays.

Another method of obtaining MoS_3 by dry means is the thermal decomposition of ammonium tetrathiomolybdate in the temperature range 190–200°C in a vacuum or inert medium[78,79,182].

It has been noted[79,112] that during the decomposition of $(NH_4)_2MoS_4$, stoichiometric MoS_2 is obtained at ~1000°C, but below 800°C the homogeneous phases MoS_{2+x} (x = 0–0.5), which have a distorted MoS_2 structure, are produced. The distortion grows with increase in x in the direction c but the lattice parameter a remains constant. Measurement of the density of such products shows that they must be considered as MoS_2 with insufficient metal, that is, they are best given the formula $Mo_{1-x}S_2$.[79]

In any of the above methods the molybdenum trisulphide obtained always contains some excess of sulphur and corresponds to the formula MoS_{3+x}, where $0 < x < 1$ and depends on the method of preparation: the value of x in the wet method reaches 0.7; in the dry method it is less[78].

Such compounds are considered either as polysulphides, whose composition is expressed, for example, by the formulae $MoS_3.S_2$ or $MoS_3.S_3$,[183] or as phases of variable composition based on MoS_3 with the addition of a certain amount of chemically unbound sulphur[78].

However, it is maintained[184–188] that molybdenum trisulphide with composition corresponding accurately to the formula $MoS_3.2H_2O$ can be obtained. For this, first 15 N ammonium sulphide or 2 N sodium sulphide is prepared by saturating the corresponding hydroxide with hydrogen sulphide below room temperature and then using the reagent obtained to treat ammonium molybdate solution. The solution of thiosalt $(NH_4)_2MoS_4$ formed is decomposed by an excess of dilute (6 N or 2 N) hydrochloric acid until completely decolorised and molybdenum sulphide is precipitated. The mixture is heated to boiling, gives a precipitate, and is filtered, the precipitate being washed successively with water, alcohol, ether, and then air is sucked through for 15 min. The precipitate, dried for 30 min in a vacuum dessicator, is reported to accurately correspond to the formula $MoS_3.2H_2O$, which enables us to use this method to determine molybdenum quantitatively. It is possible to obtain $MoSe_3$ by a similar procedure[189,190].

The thermal dissociation of air-dry preparations of $MoS_3.2H_2O$ proceeds as follows (Fig. 9). At 80–120°C the loss in weight is 1–2%. At 170–290°C the loss in weight corresponds with two molecules of water. At 290–390°C anhydrous MoS_3 is stable and at higher temperatures it is oxidised to MoO_3, which sublimes at 800°C.[187]

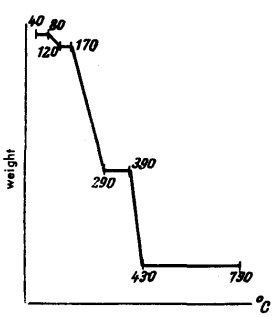


Fig. 9. Thermal dissociation curve of $MoS_3.2H_2O$.[187]

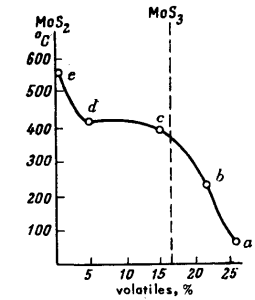


Fig. 10. Decomposition polytherm of a specimen of molybdenum trisulphide[78].

On heating in a non-oxidising atmosphere (for example, in nitrogen), molybdenum(VI) chalcogenides disproportionate into the dichalcogenide and the free chalcogen. The thermal decomposition of MoS_3 in nitrogen has the following result[78]: on heating a preparation of composition $MoS_{3+x}.yH_2O$ to 250°C there is a loss of hygroscopic and loosely bound water together with part of the sulphur in excess (Fig. 10, section a–b). Subsequently between 250° and 400°C sulphur in excess of the composition MoS_3 is removed, then the main mass of MoS_3 decomposes with simultaneous evaporation of sulphur formed during this decomposition (Fig. 10, section b–c–d). As a result, a new phase of variable composition is formed (with an excess of sulphur) based on MoS_2, which on further heating to 900–1000°C gradually loses sulphur and approaches molybdenum disulphide in composition (Fig. 10, section d–e).

Crystallisation of molybdenum disulphide has already started at 350°C, and when molybdenum trisulphide decomposes the disulphide produced crystallises as the hexagonal form. The suggestion[78] that the rhombohedral modification crystallises initially and changes into the more stable hexagonal modification as the temperature rises has not been confirmed[79].

The vapour pressure of sulphur on heating molybdenum trisulphide has been measured[80,191] between 350° and 500°C:

Temperature, °C:	355	390	418	475	480	500
Pressure, mmHg:	4.0	28.8	178.6	250	313	980

There is a difference of opinion about the reversibility of the process:[192]

$$MoS_3 \rightleftarrows MoS_2 + S.$$

For long it was thought that the decomposition of molybdenum trisulphide is reversible and that in the range 350–400°C there is an equilibrium with the disulphide[80]. However, Biltz and Köcher[145] showed the thermodynamic instability of molybdenum trisulphide. Despite this, some investigators tend to assume that it is possible to obtain the trisulphide by heating the disulphide with sulphur, if the reaction is carried out over several days at 400°.[53] Probably, such a reaction can be brought about by selecting suitable conditions.

In this connection, work[193] on the preparation of tantalum triselenide by direct synthesis from the elements is of interest. The authors[193] consider that with very slow cooling (~250 h) of the reaction products, heated to 820°C,

tantalum triselenide (which dissociates at 780°C) can be formed according to the equation:

$$TaSe_3 + Se \rightleftarrows TaSe_4.$$

They also obtained[193] tantalum trisulphide by heating the disulphide with sulphur for a week at 450–500°C.

It is interesting that tungsten trisulphide was obtained by heating the disulphide in sulphur vapour[194]. In view of the great similarity between the chalcogenides of molybdenum and tungsten, it seems quite probable that there would be similar results with the molybdenum chalcogenides.

On heating in hydrogen, the molybdenum(VI) chalcogenides are reduced to the dichalcogenides. In hydrogen selenide $MoSe_3$ does not change composition[60]. On heating in air, dry molybdenum triselenide is stable up to 410°C but at higher temperatures it is oxidised to MoO_3.[190]

The molybdenum(VI) chalcogenides are amorphous to X-rays. Evidently the chemical bond in molybdenum trisulphide is formed by d^2sp^3 hybridisation[104].

Molybdenum trisulphide readily dissolves in *aqua regia*, ammonium sulphide, and in alkali metal sulphides; it also dissolves in alkalis on heating[21]. On fusing the trisulphide with sodium carbonate the reaction is[37]:

$$MoS_3 + 2\,Na_2CO_3 \rightarrow Na_2MoO_2S_2 + Na_2S + 2\,CO_2.$$

Even in the cold molybdenum trisulphide dissolves in alkali metal sulphides and selenides, in concentrated alkali solutions, and even in concentrated ammonia. Molybdenum triselenide dissolves in concentrated sulphuric acid on heating[60].

It is interesting to note that dissolution of molybdenum triselenide, like the molybdenum(V) chalcogenides, is almost always accompanied by coloration of the solutions with a rich hue.

Molybdenum triselenide is a rather unstable compound. It reacts readily with many oxidants, but not with organic acids[60].

Molybdenum tritelluride has not yet been obtained. Apparently this compound is still more unstable than molybdenum triselenide.

The magnetic susceptibility of molybdenum trisulphide powder at 15°C is 0.361×10^{-6}.[195]

Oxide sulphides of molybdenum(VI) are known. MoO_2S is obtained by the reaction of MoO_2Cl_2 with Na_2S in alcoholic medium by the reaction[37]:

$$MoO_2Cl_2 + Na_2S \rightarrow MoO_2S + 2\,NaCl.$$

The MoO_2Cl_2 is obtained by passing dry gaseous hydrogen chloride over MoO_3 at 180°C; the alcoholic solution of the oxide chloride is kept in an atmosphere of carbon dioxide. The brown-black precipitate of MoO_2S, which resembles MoS_3, is filtered off, washed well with water (until there is no alkaline reaction), and dried in a vacuum.

There has been a report[196] of the preparation of $MoOS_2$ by the thermal dissociation of $(NH_4)_2MoO_2S_2$ in nitrogen at 300–400°C. As was found later, the decomposition of ammonium oxothiomolybdate under these conditions does not give an oxide sulphide[68]. The final product of the reaction is molybdenum disulphide with MoO_2 as impurity. Romanowski[68] has confirmed this not only by chemical analysis (which was used in the earlier work[196]) but also by X-ray and thermographic studies.

The oxide sulphides $MoO_3.2MoS_3.9H_2O$ and $MoS_3.5MoO_3.6.5H_2O$ are also known[39]. The method of obtaining these compounds consists in the reaction of solutions of Na_2MoO_4 and Na_2S followed by neutralisation with hydrochloric acid to pH 4.5. Then the mixture is heated to 90°C and held there for an hour with constant stirring, after which the solution and precipitate are kept another 12 h in a thermostat at 25° ± 0.1°C. The compounds are washed with alcohol and ether and dried at 140°C.

Particular note should be made that in these preparations the atomic ratio Mo : S plays an important part. Thus a pale brown oxide sulphide of composition $MoO_3.2MoS_3.9H_2O$ is obtained at Mo : S = 1 : 2 and 1 : 1 and the green $MoS_3.5MoO_3.6.5H_2O$ ratio at Mo : S = 2 : 1, 1.75 : 1, and 1.5 : 1. At Mo : S = 1 : 3 or over, MoS_3 is formed.

The oxide sulphides $MoO_2S.3H_2O$ and $MoOS_2.3H_2O$ are obtained by saturating a molybdate solution at pH 8.6 with hydrogen sulphide for 30 min and 12 h respectively, washing the precipitate with alcohol, and drying. On heating them to 200°C almost all the crystallisation water is lost and at higher temperatures they start to decompose[38].

Oxide compounds have not been obtained for molybdenum triselenide.

Only two molybdenum chalcogenide halides have been obtained: $Mo_5S_5Cl_9$ and $MoSCl_2$. The first of these is obtained on passing S_2Cl_2 vapour in a gentle stream of carbon dioxide over incandescent molybdenum powder. $Mo_5S_8Cl_9$ is formed as a red-brown amorphous sublimate, stable in air. It is insoluble in water and alkalis but dissolves completely in concentrated nitric acid[41].

$MoSCl_2$ was observed in the products of the chlorination of molybdenum disulphide at ~ 400°.[40]

Sulphides richer in sulphur than molybdenum trisulphide have been described[21,197,198]. Thus sulphides of the approximate composition MoS_4 and MoS_6 are obtained during the decomposition of alkali metal thiomolybdates with acids (hydrochloric or sulphuric). The compounds are insoluble at ordinary temperatures in water and acids but dissolve in alkalis and alkali metal sulphides. The authors[198] also regard such higher sulphides as anhydrides of perthio-acids of molybdenum. However, in view of insufficient experimental facts, the physicochemical properties of these products have hardly been studied at all and the homogeneity of the phases has not been established.

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Transition metal chemistry is now developing very rapidly. A series of new facts have now been obtained which are interesting not only from the practical aspect but are also of great importance theoretically. Therefore the chalcogenides of such a typical transition metal as molybdenum are undoubtedly of theoretical interest and their detailed study allows us to hope for new results of practical importance.

Study of the electrical, thermoelectric, magnetic, thermodynamic, and other properties of the transition metal chalcogenides has shown that "transition metal–chalcogen" systems are extremely complex. The tendency of chalcogenides to form compounds of non-stoichiometric composition has set the task of finding the reason for this departure, since even insignificant changes in composition lead to essential changes in some of the physical properties. Since the non-stoichiometry of the compounds is

the result of defects in the crystal lattice, the investigation of the chalcogenides is directed first to the determination of the crystal structure, to revealing the fine character of the interconnection between chemical impurities and lattice defects, and between the structure of the molecule and the physical properties of the substance.

The crystal structure of the molybdenum chalcogenides has been studied most fully only for the molybdenum(IV) compounds. However, the polymorphism of MoS_2 and the various interpretations of this phenomenon again emphasise the insufficiency of our knowledge in this region.

The information about the structure of Mo_2S_3 is little and contradictory. The structural study of the lower molybdenum selenide and telluride is restricted to the powder method. Therefore detailed structural investigation of the lower chalcogenides of molybdenum is one of the first tasks.

Data about the non-stoichiometric nature of the phases in the molybdenum–chalcogen systems confirms the necessity for a thorough study of the non-stoichiometric molybdenum chalcogenides.

The detailed determination of the structure of the compounds and the lattice defects, and of the regions and conditions of existence of the phases, requires modern physicochemical methods for the study of equilibrium diagrams. The volatility of the components and the decomposition of the compounds before melting create additional difficulties in the study of molybdenum–chalcogen systems. However, without knowledge of the physicochemical data it is impossible to correctly select methods of preparation especially in making materials suitable for semiconductor purposes. Therefore future investigation of the molybdenum chalcogenides should be directed above all to the detailed study of the physicochemical properties of systems which include these compounds.

Since the molybdenum dichalcogenides are widely used as thermoelectric materials their study in this direction is extremely promising. Good thermoelectric properties can be expected from various combinations of MoS_2, $MoSe_2$, and $MoTe_2$ with other transition metal chalcogenides.

We consider that the known molybdenum chalcogenides, oxide chalcogenides, and chalcogenide halides are only the first representatives of this class of materials. Molybdenum is known to be a rather reactive element. The variety of its chemical properties, expressed above all in its ability to vary its valency, suggest that the systematic investigation of the molybdenum chalcogenides will lead to a whole series of new compounds, not only of theoretical interest but also important for practical use.

Compounds in which the molybdenum has a lower valency should be especially reactive. The oxidation of molybdenum to higher valencies uncovers wide prospects for the preparation of new mixed compounds.

The different molybdenum compounds show greatest stability at different oxidation states. Thus in the compounds with oxygen or fluorine the most stable valency of molybdenum is six (MoO_3 and MoF_6); with chlorine, five ($MoCl_5$); with sulphur, four (MoS_2); with bromine and iodine, the most stable valency is apparently even lower. Such a selectivity of the valency of molybdenum in its compounds with different non-metals can be used to obtain new stable mixed compounds with a different degree of oxidation.

The chemical properties of the molybdenum chalcogenides have been quite inadequately investigated. The behaviour of the compounds in alkalis and acids has been described only qualitatively. Such an interesting problem as the solubility in salts has hardly received any attention. And yet here it is possible to obtain interesting results, to find possible paths for making new compounds, to find mechanisms for some reactions of molybdenum which are important to chemists.

There is great interest in carrying out the reactions in non-aqueous solvents. Such solvents as liquid ammonia, sulphur dioxide, dinitrogen tetroxide, nitrosyl chloride, hydrogen fluoride, bromine, interhalogen compounds, etc. unconditionally give rich material for theoretical investigations and allow a preparative route to be found for compounds with specially intended specific properties.

The study of the behaviour of the molybdenum chalcogenides on heating acquires special value in connection with the possibility of using them in thermoelectric assemblies. Therefore extensive thermographic analysis of the molybdenum chalcogenides in various media is urgently required.

What has been stated undoubtedly does not exhaust all the tasks which are presented by the chemistry of the molybdenum chalcogenides. However, the problems listed are the most pressing and their solution can be expected to give promising theoretical and practical information.

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KINETICS OF RECOMBINATION AND DISPROPORTIONATION REACTIONS OF ALKYL RADICALS

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The present review is an attempt to collect and systematise information from numerous Russian and non-Russian papers on the kinetic study of recombination and disproportionation reactions of free radicals.

Recombination and disproportionation of alkyl radicals

$$R_1+R_2 \begin{cases} \longrightarrow R_1R_2 & (1) \\ \longrightarrow P+O, & (2) \end{cases}$$

(R_1 and R_2 are alkyl radicals, P is a paraffin molecule, and O is an olefin molecule) are the main types of reactions in which chains are broken, or free valencies disappear, in numerous organic reactions that proceed by a radical chain mechanism in the gas or liquid phase. On the other hand, these reactions are thermodynamically linked with the dissociation of alkanes and the molecular dismutation of alkanes and alkenes, which are possible routes to radical initiation in conversions of hydrocarbons at high temperatures. Actually, the radical chain mechanism results from the competition between these reactions and chain-propagation reactions.

In the experimental study of substitution reactions

$$R + M \rightarrow RH + R_1, \quad (3)$$

the difficulty of setting up an experimental model of reaction (3) is encountered, since under experimental conditions with sufficiently complicated radicals (beginning with C_2H_5), reactions (1) and (2) occur to a great extent, and these require virtually no activation energy. This makes difficult the determination of the absolute rate constant of reaction (3) from experimental results. However, the relative value of the rate constant of reaction (3) may be determined experimentally, when it is expressed in the form of the rate constants of the recombination k_1 and disproportionation k_2 of radicals. The rate of disappearance of radicals by recombination and disproportionation in reactions (1) and (2) is

$$W = (k_1 + k_2)(R)^2. \quad (4)$$

Eliminating the concentration of radicals (R) from Eqn. (4) and Eqn. (5) for the rate of reaction (3):

$$W_3 = k_3(R)(M), \quad (5)$$

we obtain the relation

$$\frac{k_3}{(k_1+k_2)^{\frac{1}{2}}} = \frac{W_3}{W^{\frac{1}{2}}(M)}. \quad (6)$$

Since the right-hand side of Eqn. (6) contains values that can be calculated from the experimental kinetic curves for the accumulation of products (RH, R_1R_2, P, O) and for the disappearance of M, the relative value of the rate constant of reaction (3) can be calculated from experimental results.

As will be seen, by comparing reactions of the same radical R with different molecules it is possible to determine the relative values of the rate constants of radical reactions (3) without finding the concentrations of free radicals (R), which up to now has presented considerable difficulties. The essential feature of this determination forms the basis of the now well developed method of competitive reactions[1,2]. In the simplest type in the method of competitive reactions we are concerned with competing reactions of the same order, for example

$$R + M_1 = RM_1, \quad (7)$$

$$R + M_2 = RM_2. \quad (8)$$

The ratio of the rate constants of reactions (7) and (8)

$$\frac{k_7}{k_8} = \frac{W_7(M_2)}{W_8(M_1)}, \quad (9)$$

is determined from experimental measurements of the reaction rates W_7 and W_8 and the concentrations of the molecules taking part in the reactions. If the value of one of the rate constants (k_7 or k_8) can be determined (or calculated) by some independent method, the absolute value of the other constant can be determined from Eqn. (9).

However, it is not always possible successfully to choose a suitable competing reaction, and then Eqn. (6) must be used to determine the absolute rate constant of reaction (3). The solution of this problem requires independent experiments to measure absolute rate constants of the radical recombination (1) and disproportionation (2) reactions; at present these experiments present serious difficulties and must be supplemented by theoretical calculations.

Experimental difficulties are one of the reasons for the view long held that radical recombination reactions occur with every collision[3]. It should be mentioned that even

now in many experimental papers dealing with radical recombination reactions it is assumed that $k = 10^{14}$ mole^{-1} × × cm^3 s^{-1} (i.e. the steric factor $s = 1$ and $E = 0$)[4]†.

However, although the absence of a true activation energy E has been confirmed by numerous experimental results, the assumption that every collision is effective can be shown to be doubtful. This is confirmed by the fact that the steric factors for the addition of H atoms to alkenes, and also the factors for addition and replacement reactions of H and CH_3 radicals with various molecules (alkanes and alkenes), calculated by the transition-state method as applied to radical reactions[5,6,7], have low values. It may therefore be assumed that recombination reactions of CH_3, or more complex radicals, must also have low steric factors; otherwise, it would have to be accepted that reactions in which two free valencies disappear have special steric features compared with radical replacement reactions, in which the free valency is retained, but there are no grounds for this[8]. Moreover, if the preexponential factors A of the rate constants of recombination reactions are taken as equal to 10^{14} mole^{-1} cm^3 × × s^{-1}, examination of the frequency factors of decomposition reactions on the basis of entropy changes leads to values that are too high for the preexponential factors (from 10^{17} s^{-1} for n-alkyl radicals to 10^{20} s^{-1} for t-butyl radicals[4,9]). Interpretation of the negative temperature coefficient found for the rate of recombination of CH_3 radicals[3] also unambiguously indicates that the steric factor s is less than unity and its value decreases with increase of temperature[10].

Approximate evaluation of steric factors for recombination reactions of the simplest radicals shows that their values are less than unity even for the recombination of H atoms and CH_3 radicals (900°K)[8]. If it is assumed that ternary collisions are necessary for the successful recombination of these particles, as in the combination of hydrogen atoms, then the steric factor will be still lower. When one of the recombining H atoms is replaced by a CH_3 radical, the steric factor of the recombination reaction decreases at first sharply, but then more gradually as the radicals become more complex (C_2H_5, C_3H_7). In the recombination of CH_3 radicals, the steric factor decreases still further, by one order of magnitude in comparison with its value in the H + CH_3 reaction. However, calculation gives a lower value (10^{-5}) than that found experimentally ($\sim 10^{-3}$) by Brodskii[11].

The calculation of the absolute rate constants of reactions (1) and (2), and especially the preexponents of these reactions, is therefore of interest, since unfounded assumptions connected with a difference of several orders between the preexponents of reactions (1), (2), and (3) lead to the competing relations between different radical reactions appearing in a distorted light. However, we shall first examine somewhat more widely the question of the calculation of the kinetic parameters of bimolecular reactions, since recombination and disproportionation reactions belong to this class.

The calculation of the rate constants of bimolecular reactions must be based on a detailed analysis of the collision process between the particles and the accompanying redistribution of energy, and it is complicated by the fact that the interaction forces between the particles have been little studied. This calculation of intermolecular forces can only be made for a small number of the simplest atoms and molecules. It is virtually impossible with complex particles, since their electronic molecular wave functions and potential energy surfaces are not known with sufficient accuracy. Therefore, only the approximate calculation of the reaction rate constant on the basis of a simplified collision model can be considered; quantum-mechanical methods of calculating the cross section may be used for these. One of these approximate calculations was made by Bauer and Wu for the exchange reaction $H_2 + X = HX + H$, where X is a Cl or Br atom[12]; an approximate value of 10^{-2} (300°K) was found for the steric factors of these reactions, which is in good agreement with calculations by the activated-complex method[8] and also with experimental results[13].

In recent years electronic computers are being increasingly used for quantum-mechanical calculations. However, the calculations could only be carried out in the simplest of cases and with approximate methods and models. A number of papers deal with the computer calculation of the probabilities of exchange reactions AB + C = = A + BC, which has permitted a more detailed study of the effect of vibrational excitation of the initial molecule on the effective activation energy (minimal initial translational energy necessary for the reaction to occur)[14,15].

The question of the calculation of the rate constants of bimolecular reactions on the basis of quantum-mechanical collision theory has been considered by Eliason and Hirschfelder[16]; by making a number of assumptions, they related the rate constant of a bimolecular reaction to the reaction cross section by means of a Laplace transformation, and they obtained an expression in terms of transition-state theory.

Attempts have also been made to calculate the rate constant of an elementary bimolecular reaction without making the assumption of equilibrium between the activated complex and the starting molecules[17,18]; the results are approximately equal to those obtained by transition-state theory.

Recently, phenomenological and statistical thermodynamics of irreversible processes are becoming more widely used in kinetic investigations. An important step in the construction of a logical theory of irreversible microscopic processes is the deduction of general expressions for kinetic coefficients from correlation functions[19]. However, their application to chemically reacting systems meets with great mathematical difficulties. Thus, a more nearly correct calculation of the rate constant of bimolecular reactions encounters serious mathematical difficulties, and a number of assumptions leads to a result similar to that obtained by transition-state theory[20,21]. The activated-complex theory makes it possible to determine the steric factor in the expression for the preexponential factor of the rate constant ($A = sZ$), which for bimolecular reactions has the form[5]:

$$s = \gamma \frac{kT}{h} \frac{1}{Z} \frac{Q^*}{Q_A Q_B} \exp\left[-\frac{1}{2} + T \frac{d}{dT} \ln\left(T \frac{Q^*}{Q_A Q_B}\right)\right] \quad (10$$

(the generally accepted symbols have been used in this equation[7]; in what follows it is assumed that $\gamma = 1$).

† For this reason, in the method of competing reactions for studying the kinetics of reactions in which radicals are replaced by various organic molecules, the radical recombination reaction was used as a convenient standard of comparison, since then the relative values of the steric factors and activation energies agree with their absolute values.

Approximation expressions for the temperature coefficient of s for reactions in which complex particles participate may be obtained[7,22] by logarithmic differentiation of Eqn. (10):

$$s_T/s_{T_1} = (T_1/T)^{3.5} \quad (11)$$

and for reactions in which H atoms participate:

$$s_T/s_{T_1} = (T_1/T)^2. \quad (12)$$

In the transition from higher to lower temperatures (900–300°K) the steric factors of the corresponding reactions increase within the limits of two orders (for CH_3 and more complex particles) or one order (for H atoms). Experimental results obtained by the study of recombination of CH_3 radicals confirm this conclusion[3,10].

Because of the absence of spectroscopic data, the calculation of the rotational and vibrational partition functions of radicals and activated complex required by formula (10) meets with considerable difficulties. The necessary assumptions that enable satisfactory results to be obtained have previously been discussed in detail[7]. The results of calculation of steric factors of addition and replacement reactions of H atoms and CH_3 radicals with saturated and unsaturated hydrocarbons on the basis of Eqn. (10) leads to good agreement with experiment[7,23]. In later papers by non-Russian authors, preexponential factors in reactions between the simplest molecules and radicals have been evaluated in the same way.

The preexponential factors for twelve bimolecular reactions between simple inorganic molecules and radicals (including the atoms N, O, F, Cl) have been calculated by the transition-state method by Herschbach and coworkers[24]. In these reactions, the number of atoms in the activated complex did not exceed 5 or 6, and its structural and mechanical properties were calculated from the properties of the initial and final molecules. For the reaction $NO + O_3 = NO_2 + O_2$ the normal vibrational frequencies for the complex $NO{-}O_3$ were calculated from the assumed geometry and the force constants of NO_2 and O_3 molecules. The values of the steric factors found for these reactions were low (10^{-1}–10^{-3}) and are in satisfactory agreement with experimental results‡; however, usually the calculated preexponents were less than those obtained experimentally, which confirms the necessity of regarding the activated complex as a molecule in which a somewhat elongated bond is being formed[21].

In a number of reactions in which a hydrogen atom is detached ($R + M \rightarrow RH + R_1$; R = H, CH_3, CD_3, Br) the bonds formed in the activated state were assumed to be longer than those in the corresponding hydrocarbons; in finding the length of the bonds formed the authors[25,26] followed Pauling's empirical rule[27] for the relation between the covalent radii of bonds and their order:

$$R(1) - R(n) = 0.3 \log n, \quad (13)$$

where $R(1)$ is the radius of the corresponding single bond, $R(n)$ is the radius of the bond formed, which by hypothesis is always considered to be a bond of half order ($n = \frac{1}{2}$)[25,26].

‡ The preexponential factors are also calculated by making an analogy between the entropies of the activated complexes of the reactions considered and the corresponding hydrocarbon molecules similar to them in structure, but the results are not always confirmed by experiment[24].

Formula (13) shows that the length of the C–C bond in the activated complex increases by about 0.18 Å.§

The application of Pauling's empirical rule (13) enabled the structure of the activated complexes to be determined and Q_{rot} to be approximately calculated (in the calculation it was assumed that the H atoms are localised in the nuclei of the C atom with which they are linked).

The vibrational partition function has been approximately evaluated[24]. On the basis of these and a number of other assumptions, the preexponential factors for reactions in which H atoms are abstracted have been found within a factor of ten. Values of the steric factor (10^{-1}–10^{-3}) in a number of available instances are in good agreement with those found by calculation from formula (10) and by experiment[23].

The preexponential factor of a reaction of the type $RH + Cl = R + HCl$ (where R = CH_3 (has been obtained from partition functions calculated by the classical method[29] and is in agreement with the experimental value¶. This method of calculation has the advantage that it requires less detailed information on reagents and activated complexes; in particular, and this is very important, data on the normal vibrational frequencies of the reagents and the activated complex are not required. Calculation of the classical partition function, of course, requires a knowledge of the potential energy surface. The authors assume that it corresponds approximately with the potential energy surface for the reaction $H_2 + Cl = HCl + H$. The bonds in the activated complex (C–H and H–Cl) were assumed to be longer than in the corresponding compounds, in accordance with Pauling's empirical rule (see above). The preexponential factor of this reaction was evaluated on the basis of these assumptions.

The method of calculating preexponential factors considered has been generalised for reactions of the type $CF_3 + RH \rightarrow CF_3H + R$, (where RH = C_2H_6, n-C_3H_8, n-C_4H_{10}) and the case has been considered in which the activated complex may be represented as an aggregate of three rigidly linked groups, each with its own reaction centre (three-centre problem X–Y–Z)[31]. Information on the potential energy surface may be obtained from the force constants of the particles. The preexponential factor A may then be expressed in terms of the force constants and other characteristics of the reacting particles and the activated complex (bond length, symmetry number, etc.). The unknown valence force constants for the selected geometric structure of the activated complex were roughly evaluated[31] by Badger's empirical rule[32], and the deformation force constants were obtained from a comparison with simpler known examples. The calculated preexponents of these reactions agree with the experimental values; it has been shown that the quantum correction in this classical evaluation of the partition function is not great, being less than 1.4 when $\omega < 1000$ cm^{-1} at 400°K.[31]

In radical polymerisation reactions a number of questions may be interpreted in the light of the calculations of steric factors[33]. It has been found that the steric factor of the

§ This rule has also been used for other types of bonds[26,28,29].

¶ Some divergencies from experimental results which have been found by Knox and Trotman-Dickenson in the evaluation of the preexponents of the rate constants of analogous reactions on the basis of transition-state theory are due to a somewhat simplified approach to the calculation of the partition functions of the initial particles and activated complexes[20].

propagating reaction in the molecular and radical polymerisation of ethylene greatly diminishes only in the early stages of polymerisation, but then the formation of trimer, tetramer, etc. occurs at a constant value of s (10^{-5}–10^{-6}). Similar relationships are observed in radical polymerisation reactions of propene, in which the steric factor of initial chain growth is particularly low (10^{-7}–10^{-9}). This explains why polymerisation of unsaturated molecules is frequently interrupted at the dimerisation stage[34], and also indicates that polymers of different chain length are equally reactive[35]. A comparison of the steric factors in radical and molecular polymerisations† shows that under the same conditions radical polymerisation must proceed more rapidly than molecular, because of the low activation energy in the propagating reaction (4–7 kcal instead of 38 kcal for molecular polymerisation).

Thus, numerous calculations of preexponential factors of addition and substitution reactions between simple molecules and radicals based on transition-state theory show that these reactions have low steric factors ($s \simeq \simeq 10^{-1}$–10^{-5}), in agreement with experimental results.

We shall now consider the kinetic characteristics of radical recombination and disproportionation reactions[23,37-43].

A current model for radical recombination reactions enables activation energies to be calculated and also permits a more nearly correct calculation of steric factors of these reactions, and rate constants can be evaluated from these.

Let us consider the recombination reaction A + B = AB. If A and B are atoms, the potential energy surface is two--dimensional, i.e. it is a curve similar to a Morse curve. Since the approaching atoms have a relative angular momentum, it is still necessary to calculate their centrifugal energy of rotation for each quantum state and for each distance between them. From this the position of the activated state on the potential energy surface can be determined; the energy maximum equal to the sum of the rotational and potential energies will correspond to this position. From this and the most probable value of the rotational quantum number j^* for the activated complex, the most probable interatomic distance (effective collision diameter) in the transition state can be calculated. As calculations show[21], the value of the effective collision diameter r^* is several times greater than the equilibrium interatomic distance in the molecule AB (for H–H, $r^* = = 4$–5 Å), and therefore the energy of dispersion interaction may be used as an approximate evaluation of the energy barrier. The rate constants of recombination reactions of some simple radicals have been calculated from the theory of absolute reaction rates by the use of this method with some assumptions[44-47].

The steric factors of radical recombination reactions can be calculated from more detailed information on the activated state, and the activation energies can also be calculated by the solution of two transcendental simultaneous equations which may be obtained from the accepted model of the recombination reaction. Actually, the energy barrier E is the difference between the centrifugal energy ϵ_j and the polarisation energy ϵ_p of the approaching radicals; when account is taken of the dissociation energy of the molecule D and its vibrational energy ϵ_v the energy barrier is given by:

$$E(r, j) = \varepsilon_j - (D - \varepsilon_v) - \varepsilon_p. \quad (14)$$

In the activated state Eqn. (14) has a maximum, that is, the following condition holds:

$$\frac{\partial E(r, j)}{\partial r} = 0,$$

from which the equation for r follows:

$$r = r(j). \quad (15)$$

The probability of the activated state $\omega(r, j)$ is calculated in the usual manner

$$\omega(r, j) = (2j+1)\exp\left(-\frac{E}{kT}\right).$$

The most probable values of j^* for the activated complex may be calculated from the condition

$$\frac{\partial \omega(r, j)}{\partial j} = 0 \quad (16)$$

and then the interatomic distances r^* of the separating particles in the transition state may be evaluated. The height of the barrier (Eqn. 14) that must be overcome by radicals to form a stable molecule may be evaluated from the values of r^* and j^* found. The parameters in Eqn. (15) and Eqn. (16) characterise the physicochemical properties of the radicals (their polarisabilities and ionisation potentials) and the bond of the activated complex formed (its dissociation energy, vibrational constant, and equilibrium distance).

It is well known that free radicals have ionisation potentials that differ little from the ionisation potentials of the molecules from which they are obtained. Concordant values of the ionisation potentials of many alkyl radicals have been obtained by electron-impact, photoionisation, and other methods[48]. Since the occupied electronic radical orbitals are not lower than the orbitals of the related molecules, it may be assumed that they are geometrically similar to one another[49]. This suggests that the polarisability of the radical is intermediate between the polarisabilities of the alkane and alkene molecules (the values for the latter are close[50]).

$$\alpha(R) \simeq \frac{\alpha(C_nH_{2n+2}) + \alpha(C_nH_{2n})}{2}.$$

Values of the dissociation energy of the corresponding bonds may be found in the literature[48,51]. The numerical value of the vibrational force constant differs little from the stretching vibration of the corresponding C–C (or C–H) bond. Data required for calculating the parameters in the equations above, and also the parameters themselves, have been published[23,37].

Table 1 is concerned with recombination reactions, mainly of alkyl radicals.

The transcendental Eqns. (15) and (16) have been solved on a Ural-1 electronic computer. The following conclusions may be drawn from the results obtained.

1. With regard to the energy barrier, radicals entering into the reactions are practically equivalent, since the activation energy of the recombination reaction E is 200–300 cal.

† Low steric factors in polymer chain-lengthening reactions mean low preexponents, and therefore reaction rates are not so high, although the reactions have low activation energies. Recently it has been found[36] that in methyl methacrylate polymerisation reactions the steric factor is 10^{-4}.

TABLE 1. Steric factors and rate constants for the recombination and disproportionation of alkyl radicals.

Reaction No.	Reaction	900°K				300°K			
		recombination		disproportionation		recombination		disproportionation	
		s_1	k_1	s_2	k_2	s_1	k_1	s_2	k_2
1	$H+CH_3$	$2.3\ 10^{-2}$	$2.0\ 10^{-11}$	—	—	$3.6\ 10^{-1}$	$1.8\ 10^{-10}$	—	—
2	$H+C_2H_5$	$5.5\ 10^{-3}$	$7.3\ 10^{-12}$	$2.7\ 10^{-3}$	$3.5\ 10^{-12}$	$8.5\ 10^{-2}$	$6.6\ 10^{-11}$	$2.4\ 10^{-2}$	$1.9\ 10^{-11}$
3	$H+C_3H_7$	$1.7\ 10^{-3}$	$3.1\ 10^{-12}$	$1.1\ 10^{-3}$	$2.1\ 10^{-12}$	$2.6\ 10^{-2}$	$2.8\ 10^{-11}$	$1.0\ 10^{-2}$	$1.1\ 10^{-11}$
4	$H+C_4H_9$	$5.9\ 10^{-4}$	$1.2\ 10^{-12}$	$5.4\ 10^{-4}$	$1.0\ 10^{-12}$	$9.2\ 10^{-3}$	$1.1\ 10^{-11}$	$4.9\ 10^{-3}$	$5.9\ 10^{-12}$
5	CH_3+CH_3	$1.1\ 10^{-3}$	$4.9\ 10^{-13}$	—	—	$9.1\ 10^{-2}$	$2.3\ 10^{-11}$	—	—
6	$CH_3+C_2H_5$	$2.3\ 10^{-4}$	$1.3\ 10^{-13}$	$3.5\ 10^{-5}$	$1.9\ 10^{-14}$	$1.9\ 10^{-2}$	$6.1\ 10^{-12}$	$1.7\ 10^{-3}$	$5.2\ 10^{-13}$
7	$CH_3+C_3H_7$	$5.6\ 10^{-5}$	$3.8\ 10^{-14}$	$7.7\ 10^{-6}$	$5.3\ 10^{-15}$	$4.5\ 10^{-3}$	$1.8\ 10^{-12}$	$3.6\ 10^{-4}$	$1.5\ 10^{-13}$
8	$CH_3+C_4H_9$	$2.2\ 10^{-5}$	$1.5\ 10^{-14}$	$6.4\ 10^{-6}$	$4.4\ 10^{-15}$	$1.8\ 10^{-3}$	$7.0\ 10^{-13}$	$3.0\ 10^{-4}$	$1.2\ 10^{-13}$
9	$CH_3+C_5H_{11}$	$1.2\ 10^{-5}$	$9.5\ 10^{-15}$	$3.5\ 10^{-6}$	$2.7\ 10^{-15}$	$9.6\ 10^{-4}$	$4.5\ 10^{-13}$	$1.7\ 10^{-4}$	$7.5\ 10^{-14}$
10	$C_2H_5+C_2H_5$	$1.0\ 10^{-5}$	$6.4\ 10^{-15}$	$2.2\ 10^{-6}$	$1.4\ 10^{-15}$	$8.0\ 10^{-4}$	$3.0\ 10^{-13}$	$1.0\ 10^{-4}$	$3.9\ 10^{-14}$
11	$C_2H_5+C_3H_7$	$3.3\ 10^{-6}$	$2.5\ 10^{-15}$	$9.2\ 10^{-7}$	$6.9\ 10^{-16}$	$2.6\ 10^{-4}$	$1.2\ 10^{-13}$	$4.3\ 10^{-5}$	$1.9\ 10^{-14}$
12	$C_2H_5+C_4H_9$	$2.0\ 10^{-6}$	$1.5\ 10^{-15}$	$5.7\ 10^{-7}$	$4.2\ 10^{-16}$	$1.6\ 10^{-4}$	$7.0\ 10^{-14}$	$2.7\ 10^{-5}$	$1.1\ 10^{-14}$
13	$C_2H_5+C_5H_{11}$	$1.6\ 10^{-6}$	$1.3\ 10^{-15}$	$4.7\ 10^{-7}$	$3.7\ 10^{-16}$	$1.3\ 10^{-4}$	$6.1\ 10^{-14}$	$2.2\ 10^{-5}$	$1.0\ 10^{-14}$
14	$C_3H_7+C_3H_7$	$1.2\ 10^{-6}$	$1.0\ 10^{-15}$	$3.4\ 10^{-7}$	$2.8\ 10^{-16}$	$9.9\ 10^{-5}$	$4.7\ 10^{-14}$	$1.6\ 10^{-5}$	$7.7\ 10^{-15}$
15	$C_3H_7+C_4H_9$	$1.0\ 10^{-6}$	$8.0\ 10^{-16}$	$2.8\ 10^{-7}$	$2.3\ 10^{-16}$	$8.0\ 10^{-5}$	$3.8\ 10^{-14}$	$1.3\ 10^{-5}$	$6.2\ 10^{-15}$
16	$C_3H_7+C_5H_{11}$	$8.3\ 10^{-7}$	$7.1\ 10^{-16}$	$2.3\ 10^{-7}$	$2.0\ 10^{-16}$	$6.7\ 10^{-5}$	$3.4\ 10^{-14}$	$1.1\ 10^{-5}$	$5.5\ 10^{-15}$
17	$C_4H_9+C_4H_9$	$7.5\ 10^{-7}$	$5.6\ 10^{-16}$	$2.1\ 10^{-7}$	$1.6\ 10^{-16}$	$6.0\ 10^{-5}$	$2.6\ 10^{-14}$	$9.9\ 10^{-6}$	$4.4\ 10^{-15}$
18	$C_4H_9+C_5H_{11}$	$5.5\ 10^{-7}$	$4.5\ 10^{-16}$	$1.8\ 10^{-7}$	$1.4\ 10^{-16}$	$4.4\ 10^{-5}$	$2.1\ 10^{-14}$	$8.5\ 10^{-6}$	$3.9\ 10^{-15}$
19	$C_5H_{11}+C_5H_{11}$	$3.3\ 10^{-7}$	$2.8\ 10^{-16}$	$1.1\ 10^{-7}$	$9.4\ 10^{-17}$	$2.6\ 10^{-5}$	$1.3\ 10^{-14}$	$5.2\ 10^{-6}$	$2.6\ 10^{-15}$
20	$2iso\text{-}C_3H_7$	$2.5\ 10^{-8}$	$2.0\ 10^{-15}$	$3.7\ 10^{-8}$	$3.0\ 10^{-15}$	$2.0\ 10^{-4}$	$9.4\ 10^{-14}$	$1.7\ 10^{-4}$	$8.3\ 10^{-14}$
21	$2iso\text{-}C_4H_9$	$1.8\ 10^{-10}$	$1.3\ 10^{-19}$	$1.3\ 10^{-10}$	$1.0\ 10^{-19}$	$1.4\ 10^{-6}$	$6.1\ 10^{-18}$	$0.6\ 10^{-5}$	$2.6\ 10^{-18}$
22	$2s\text{-}C_4H_9$	$1.4\ 10^{-9}$	$1.1\ 10^{-18}$	$5.2\ 10^{-9}$	$3.9\ 10^{-18}$	$1.1\ 10^{-7}$	$5.2\ 10^{-17}$	$2.5\ 10^{-7}$	$1.1\ 10^{-16}$
23	$2t\text{-}C_4H_9$	$1.6\ 10^{-9}$	$1.2\ 10^{-18}$	$1.2\ 10^{-8}$	$0.9\ 10^{-17}$	$1.3\ 10^{-7}$	$5.6\ 10^{-17}$	$5.7\ 10^{-7}$	$2.5\ 10^{-16}$

2. The distance r^* between the radicals in the activated complex is several times greater than the distance separating the radicals in the corresponding hydrocarbon and is equal to 4–5 Å for all reactions (900°K).

3. At normal temperatures ($\sim$300°K) the value of r^* increases by about 1 Å, which increases the temperature dependence of the steric factors.

4. A change of 10–20% in the values of the parameters in Eqn. (15) and Eqn. (16) leads to virtually the same solutions, which indicates the lack of sensitivity of the equations and the possibility of using them in the calculation of kinetic characteristics.

Therefore, in the study of radical recombination reactions the preexponents of the rate constants of these reactions are particularly significant, since the exponential factor is always of the order of unity — $\exp(-E/RT) \simeq 0.7$. Here it is easy to follow the effect of the structure of the reacting particles on the change in their reactivity, since the difference between the activity of the radicals in combining is due only to a change in steric factors.

The steric factors of recombination reactions of alkyl radicals were calculated from Eqn. (10). In contrast to previous calculations[8] (the length of the bond formed in the activated complex of recombination reactions was taken to be 15–20% greater than the bond in the corresponding hydrocarbon) values of r^* obtained by solving the equations above were used. This led to a tenfold to fifteenfold increase in the steric factors compared with values previously calculated.

The results of the calculation (Table 1) show that the steric factor is of the order of unity only for the recombination of such simple radicals as H and CH_3 (300°K). At higher temperatures the value of s decreases by two orders ($s \simeq 1\times10^{-2}$). For more complex radicals in reactions of the type (H + R = HR), the value of s decreases at first by an order and then more gradually.

The value of the steric factor for the recombination of two CH_3 radicals is 9×10^{-2} (300°K), or 10^{-3} (900°K). As one of the combining radicals becomes more complex, the value of s decreases, and for the recombination of CH_3 and C_5H_{11} radicals it reaches a limiting value ($s_{300} \simeq 10^{-3}$; $s_{900} \simeq 10^{-5}$).

A similar picture is observed for the recombination of C_2H_5 radicals; the steric factors for their recombination are 8×10^{-4} (300°K) and 10^{-5} (900°K), which are lower by two orders than the factors for the recombination of two methyl radicals. For this group of reactions the value of s decreases gradually as the radicals become more complex, and the limiting value is lower than in reactions in which CH_3 radicals take part ($s_{900} \simeq 10^{-6}$, $s_{300} \simeq 10^{-4}$).

In the recombination of C_3H_7 radicals there is a slight reduction in the steric factor ($s_{300} \simeq 10^{-4}$, $s_{900} \simeq 10^{-6}$), which scarcely changes as the combining radicals become more complex.

Recombination reactions of more complex radicals have about the same values of s ($s_{300} \simeq 4\times10^{-5}$, $s_{900} \simeq 10^{-7}$).

Recombination reactions of the isomeric radicals iso-C_3H_7, s-C_4H_9, and t-C_4H_9 have lower steric factors. Evidently, this is because the branched structure of the radical inhibits the formation of the dimer.

Thus, as the reacting radicals become more complex the steric factors of their recombination reactions decrease. Therefore, more complex radicals are less reactive; the value of the steric factor may be taken as a measure of the activity of the radicals. The results of the calculation of steric factors show that the activity of free alkyl radicals decreases with increasing chain length up to a certain limit (C_3–C_4), after which there is almost no further change; secondary and tertiary radicals also show a decrease compared with primary radicals. According to Semenov[51], this is connected with the interaction of an electron of the free valency with electrons of the adjacent C–C and C–H σ-bonds. This leads to a change in the shape of the radicals and to comparatively small changes in electron density due to overlap and interaction of the electron clouds of the free electron and the electrons of the σ-bonds. It is this type of interaction that reduces the activity of alkyl radicals in the transition from CH_3 to C_4H_9, and also when hydrocarbon branching increases up to a certain limit.

The recombination rate constants were evaluated from the values found for the steric factors, numbers of binary collisions z of reacting radicals, and activation energies of these reactions; the values of these constants together

with the calculated steric factors are given in Table 1. It is of interest to compare the theoretical and experimental values of the kinetic parameters considered.

Avramenko and Postnikova [53] made a kinetic study of the recombination of the simplest CH_3 radicals at low temperatures, when the steric factor of this reaction has the low value of ~ 0.1 (the calculated value of s_{300} is 9.1×10^{-2}). As the temperature is raised, the value of the rate constant falls, because of the temperature dependence of the preexponential factor. The calculated steric factor for the recombination reaction of CH_3 radicals falls to 10^{-3} at high temperatures; this agrees with the experimental value obtained by determining the temperature dependence of the rate constant by means of tracer atoms [11].

A negative temperature dependence was also found for the recombination of CH_3 and C_2H_5 radicals in a study of the mechanism of high-temperature cracking of ethane; this indicates a low steric factor for this reaction [54]. The experimental value of the steric factor ($\sim 10^{-3}$) is close to the calculated value (2.3×10^{-4}) (Table 1).

In a number of instances the concentrations of reacting radicals have been obtained from experimental results [44,45,55]; this enables the rate of accumulation of dimer, $W = k_1(R)^2$, to be evaluated from the calculated rate constant of the radical recombination reaction. Comparison shows that the calculated rates of recombination and disproportionation of C_2H_5, C_3H_7, and C_5H_{11} radicals are in good agreement with the experimental values (Table 2).

It is interesting to study the change in the reactivity of radicals with the introduction of substituents and also with the introduction of a new partner in the recombination reaction. Theoretical examination of the recombination of CF_3 radicals, and also of the combination of CF_3 and CH_3 radicals [37], shows that these reactions are energetically similar to the reactions described above ($E \simeq 200$–300 cal, $r^* \simeq 5$ Å). The calculated steric factor for the recombination of CF_3 radicals is considerably lower (4.6×10^{-6}, 900°K) than the factor for the analogous reaction with CH_3 radicals. For the recombination of CF_3 and CH_3 radicals s has an intermediate value (5.2×10^{-4}). It follows from these results that replacement of H atoms in CH_3 radicals by F atoms (with a greater atomic volume and the more polar C–F bond) leads to a sharp reduction in the steric factor, but differences between the recombination reactions of CH_3 and CF_3 radicals have not been observed experimentally [56]. The experimental activation energy for CF_3 radicals ($E \simeq 2.1$ kcal [57]) does not agree with the value calculated from the accepted model. If it is assumed that the activation energy is low, as in other cases, a value of 10^{-2} is obtained for the steric factor, which is greater than the value found, $s \simeq 4 \times 10^{-4}$ (300°K)‡.

Experimental results show that CF_3 radicals remove hydrogen from methane and ethane molecules more easily than CH_3 radicals [59,60]. Only relative steric factors of these reactions can be determined experimentally, and since the calculated value of s for the recombination of CF_3 radicals is considerably less than that for the recombination of CH_3 radicals, this may be a simple explanation of the experimentally observed increased activity of CF_3 radicals in reactions with saturated molecules (the activation energies of both substitution reactions are close).

TABLE 2. Calculated and experimental rates of recombination and disproportionation of alkyl radicals.

$2R \rightarrow R_2(1)$, $2R \rightarrow P+O(2)$	W (molecules cm^{-3} s^{-1}) $\times 10^{-12}$											
	W_1	W_1^{exp}	W_2	W_2^{exp}	W_1	W_1^{exp}	W_2	W_2^{exp}	W_1	W_1^{exp}	W_2	W_2^{exp}
	320° K				370° K				420° K			
$C_2H_5+C_2H_5$ [44]	0.39	0.44	0.06	0.0585	20.4	24	4.55	3	2.22	2.47	0.46	3
	370° K				390° K				420° K			
$C_3H_7+C_3H_7$ [45]	46	45.4	7.8	6.2	46	42.2	—	—	59	56	10	6.6
	336° K				420° K							
$C_5H_{11}+C_5H_{11}$ [55]	1.4	0.3	0.3	0.12	2.46	—	0.56	0.23	—	—	—	—

When radicals collide, in addition to recombination, the competing process in which they are disproportionated with the formation of two molecules is observed. In disproportionation reactions, as in exchange reactions, a hydrogen atom migrates from one particle to another. However, ordinary exchange reactions are exothermic by not more than 25 kcal, but the heat given out in disproportionation reactions is considerably greater (50–60 kcal). Disproportionation reactions would therefore be expected to have a low activation energy, and as a result are encountered no less frequently than radical recombination reactions. This may be demonstrated by an experimental study of the products of these reactions, which include saturated and unsaturated molecules as well as dimer.

Free radicals are mainly obtained by photolysis or pyrolysis of suitable compounds, by mercury photosensitisation of saturated molecules, or by the addition of a hydrogen atom to an alkene. Sources of the radicals include molecules of metal alkyls, ketones, aldehydes, and also other compounds. The following reaction scheme may be used to study the mechanism and kinetics of recombination and disproportionation reactions [52,61]:

$$M + h\nu \rightarrow 2R\,(\text{or } R_1 + R_2) \qquad (17)$$

$$2R \rightarrow R_2\,(k_1)$$
$$2R \rightarrow P + O\,(k_2).$$

Clearly,

$$k_2 = \frac{W_O}{(R)^2} \text{ or } \frac{W_P}{(R)^2} \text{ and } k_1 = \frac{W_{R_2}}{(R)^2} \qquad (18)$$

$$\Delta = \frac{k_2}{k_1} = \frac{W_O}{W_{R_2}} \text{ or } \frac{W_P}{W_{R_2}}.$$

The ratio Δ may be found by analysis of the reaction products, the dimer R_2, P, or O, with subsequent determination of the rates of formation W of the corresponding compounds. However, the reaction scheme may be more complex than that considered above. Frequently alkene and alkane molecules are formed by the following reactions

$$R + M = r + RH\,(k_3) \qquad (19)$$

$$r = O + R' + X, \qquad (20)$$

where r is the radical formed by removal of a hydrogen atom from the molecule M. If at the temperatures under

‡ On the basis of experimental results on the rates of the radical recombination reactions $2CH_3 = C_2H_6$ (a), $CH_3 + CF_3 = CH_3CF_3$ (b), and $2CF_3 = C_2F_6$ (c), the relative change in activation entropy of reaction (b) in relation to reactions (a) and (c) $\Delta S_b^* - \frac{1}{2}(\Delta S_a^* - \Delta S_c^*)$ has been calculated. Calculation of this by the theory of absolute reaction rates with the use of known values of the internal rotation barriers for ethane and substituted ethanes gives a value close to the experimental ratio of the preexponents [58].

study it is still necessary to take reaction (19) into account, then

$$W_P = k_2(R)^2 + k_3(R)(M)$$
$$W_{R_2} = k_1(R)^2.$$

Therefore

$$\frac{W_P}{W_{R_2}} = \frac{k_2}{k_1} + \frac{k_3(M)}{\sqrt{k_1 W_{R_2}}}.$$

Since W_P, W_{R_2}, and (M) may be measured experimentally, the ratio Δ is found graphically using plots of W_P/W_{R_2} against (M). Extrapolation of the straight line obtained to (M) = 0 will give an intercept on the ordinate equal to k_2/k_1. Sometimes additional difficulties are encountered, because alkane and alkene molecules are formed in the initial photolytic step [52].

When radicals are formed in the presence of an excess of hydrogen atoms by addition of the latter to alkenes, the value of Δ may be found by determining the relative amounts of P and R_2 in the products, provided that the reaction $R + H_2 = RH + H$ plays an insignificant part at the experimental temperatures [62]. This method of investigation has two disadvantages [63]. The first is that a careful mass-spectrometric analysis of the dimer (which is not an easy task) must be carried out to determine which radicals are present in the reacting system. Moreover, radicals formed by the addition of H-atoms to alkenes have a considerable excess of internal energy (~ 40 kcal), which makes them unstable with regard to decomposition into simpler particles. For these reasons, results obtained by this method should be viewed critically.

Numerous experimental results that have been quoted very frequently in recent years for the ratio of the rate constants of disproportionation and recombination reactions have been obtained by a study of the systems mentioned. The main reason for the divergence of experimental values of Δ appears to be the use of different methods of initiation, leading to the production of radicals with different internal energies. The reasons for the divergence of experimental results obtained by different workers is discussed by Thynne [64].

The parameters s and E for radical disproportionation reactions have been obtained from Eqn. (18) with the use of experimental values of Δ and on the assumption [4] that each collision leading to the combination of two radicals is effective ($s = 1$, $E = 0$). Since the experimental ratios of the rate constants are of the order $1-10^{-1}$, it is concluded that the steric factors of radical disproportionation reactions are within the same limits; it is assumed that the activation energies of these reactions are approximately equal to the activation energies of recombination reactions [65]. However, it has been shown in a number of experimental and theoretical papers that s is less than unity in radical recombination reactions (Table 1). Such an approach to the numerical evaluation of the preexponential factors of disproportionation reactions on the basis of experimental values of Δ and the assumption that $k_1 = 10^{14}$ mole^{-1} cm^3 s^{-1} for all alkyl radicals is therefore unsound. In this connection, the calculation of absolute rate constants of radical disproportionation reactions and, in the first instance, more detailed evaluation of preexponential factors are of interest.

Available experimental results on radical disproportionation reactions (the systematic study of which began in the last decade) do not allow the setting up of any definitive reaction model. Combination and disproportionation reactions of deuterated ethyl radicals have been observed in the photolysis of 2,2,4,4-tetradeuterodiethyl ketone [66]; two possible mechanisms for the disproportionation of ethyl radicals were considered: the "head-to-tail" mechanism

$$CH_3-CH_2- + H-CH_2-CH_2- = C_2H_6 + C_2H_4, \quad (21)$$

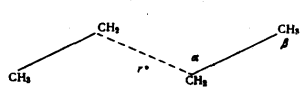
and the "head-to-head" mechanism

$$CH_3-CH_2- + H-CH-CH_3 = C_2H_6 + C_2H_4. \quad (22)$$

On the basis of a study of the isotopic composition of the products (the ethylene consisted of 90% $C_2H_2D_2$), it was concluded that the radicals preferentially disproportionate by the "head-to-tail" mechanism ($CH_3-CD_2\ldots H-CH_2-CD_2$). Similar results were obtained in the pyrolysis of the same ketone [67]. Mass-spectrophotometric analysis of the products showed that CH_3CD_2H and $CH_2=CD_2$ are mainly obtained in the disproportionation of ethyl radicals.

The possible mechanism of the disproportionation of alkyl radicals has again been discussed in a number of recent papers. Bradley draws attention to the similarity of the values of the rate constants of radical recombination and disproportionation reactions [40]. It has previously been noted that the activated complex in recombination reactions consists of two freely rotating radicals [46]. Since the rate constants of recombination and disproportionation reactions are close, it is reasonable to assume that the radicals also rotate freely in the activated complex in disproportionation reactions. From this it can be concluded that the transition states are identical. However, the "head-to-tail" mechanism cannot allow such freedom to the radicals in the activated state undergoing disproportionation, and since the energy surfaces corresponding to radical recombination reactions scarcely change with the radicals considered (this is demonstrated quantitatively by calculations of the activation energies of these reactions), it must be assumed that rearrangement of the activated molecule for disproportionation occurs after passage through the transition state. Because disproportionation is a highly exothermic process, the energy barriers to rearrangement cannot exceed the initial activation energy of the radicals, and therefore cannot be expressed experimentally as temperature coefficients of the reaction.

For the reaction between ethyl radicals Bradley considers the rearrangement of an activated molecule formed by the "head-to-head" mechanism, which has the following form in the case of radical recombination reactions:



The central C–C bond is ruptured in the reaction and a hydrogen atom is transferred from one half of the activated butane molecule to the other. The author concludes from an examination of the activated butane molecule that a β-hydrogen atom migrates to the methylene group of the other radical, and this converts the system into the reaction products, ethane and ethylene; as a result of intramolecular movements, the hydrogen in the β-position of one radical comes closer to the methylene group of the other radical than do the other hydrogen atoms. Bradley presents a number of proofs of the proposed mechanism [40].

Kerr and Trotman-Dickenson have proposed a similar explanation of the mechanism of disproportionation of alkyl

radicals[4,41]. Because of the closeness of the rate constants of reactions (1) and (2), they assume that radicals in the activated complex of disproportionation reactions are no less free than in the complex of recombination reactions. The structure of the activated complex in a "head-to-tail" disproportionation reaction does not allow such freedom to the radicals. It is considered that a dimer is formed initially and this then decomposes by a four-centre reaction. Since such dimerisation is a highly exothermic process, the activation energy required for decomposition is available.

This view of the mechanism of disproportionation of alkyl radicals has been confirmed by the work of Matsuoka and coworkers[42]. They investigated recombination and disproportionation reactions of ethyl radicals obtained by photolysis. The dependence of $\log\Delta$ of $1/T$ is linear in the temperature range -78° to + 85°C (some side reactions were excluded by the use of low temperatures). The observed negative temperature coefficient of this reaction may be explained by assuming that the radical disproportionation results from deformation vibrations of the active butane molecule which is formed by the union of two ethyl radicals. This leads to the migration of a hydrogen atom in the β-position from one radical to the methyl group of the other. This process competes with the intermolecular dispersion of energy of an incipient C–C bond which leads to butane as the product of the radical recombination reaction.

Quite recently Bradley and Rabinovitch have critically reexamined the mechanism of radical disproportionation[43]. They point out that, because of the rigidity of the activated complex, the previously accepted "head-to-tail" mechanism cannot correspond to the transition state of the disproportionation reaction, for which a looser structure is assumed. It may be assumed from the similarity between the activated complexes of radical disproportionation and recombination reactions that the corresponding saddle points are energetically and configurationally similar, and some reaction complexes may pass through both configurations. However, the experimental divergence between the values of k_1 and k_2, which differ by almost a factor of ten for most reactions of alkyl radicals, indicates that caution must be used in drawing an analogy between the mechanisms of these reactions. Moreover, possible amendments to the mechanism of radical reactions§ obviously change the existing point of view on the mechanisms of these reactions.

The well-known experimental fact that $E_{rec} - E_{dis} \simeq 0$ may be used to evaluate the rate constants of disproportionation reactions of alkyl radicals[65]. It is also assumed that the transition state in a disproportionation reaction is formed by a "head-to-head" mechanism; the reaction products then result from the transfer of a hydrogen atom in the β-position from one radical to the other[40]. Moreover, by analogy with exchange reactions (the distance between the particles in the activated complex has been found theoretically and experimentally for the simplest of these reactions[20,21]), it has been assumed that for migration of a hydrogen atom the disproportionating radicals must approach one another to a distance r^*, which is of the same order as the length of the interatomic bond in the corresponding hydrocarbon.

§ Rice recently pointed out another possible mechanism for radical recombination reactions, which consists in the coupling of combining radicals by means of three-centre H-atom bonds[68].

The rate constants for the disproportionation of alkyl radicals have been calculated from Eqn. (10) with the use of these assumptions. The data necessary for the calculation of the preexponents of these reactions have been published[23,37,39].

The results obtained show that disproportionation reactions have lower steric factors and rate constants than recombination reactions (Table 1). The reaction between a hydrogen atom and an ethyl radical, which is one of the simplest disproportionation reactions, has a steric factor much less than unity (2.4×10^{-2}) at room temperature. Disproportionation reactions in which hydrogen and more complex radicals participate have lower steric factors. At higher temperatures ($\sim$ 900°K) these values of s become still lower (Table 1), in accordance with Eqn. (11).

Replacement of a hydrogen atom by a CH_3 radical in the reaction between methyl and ethyl radicals leads to a reduction of the steric factor by about one order (1.7×10^{-3}, Table 1). As the reacting radicals become more complex (reactions 6–9, Table 1), the steric factor decreases more gradually, reaching a limiting value in these reactions of $\sim 10^{-4}$ (300°K) or $\sim 4\times10^{-6}$ (900°K).

A similar situation is observed with ethyl radicals (see reactions 10–13 in Table 1); the steric factor for the disproportionation of ethyl radicals is 10^{-4}.

We have made supplementary calculations in connection with the discussion above on the possible mechanism of disproportionation of ethyl radicals. Different directions of approach of two ethyl radicals which may disproportionate by the "head-to-tail" mechanism, and local changes of up to 20% in bond lengths and angles change the final result by less than a factor of 1.5. Similar calculations on the basis of the "head-to-head" mechanism, which is also accepted for other radical disproportionation reactions, lead to virtually the same values of the rotational partition coefficient of the activated complex. Thus, the difference between these two mechanisms cannot materially affect the value of the preexponential factors[37].

For reactions in which more complex radicals participate (reactions 14–19 in Table 1), the values of the steric factors scarcely change from one disproportionation reaction to another ($s_{300} = 10^{-5}$ and $s_{900} = 10^{-7}$). These may be considered as limiting values of the steric factors, which no longer depend on the complexity of the disproportionating radicals. The reduction in the reactivity of isomeric radicals (Table 1) appears to be due to the partial screening of the free valency caused by the branched structure of the radicals.

The rate constants of disproportionation reactions have been evaluated (Table 1) from calculated values of the steric factors and the numbers of binary collisions with the use of the assumption mentioned above on the values of the activation energies of these reactions.

When more extensive experimental results have been obtained, it should be possible to put forward a more precise mechanism for radical disproportionation reactions and to examine the energy barrier in these reactions both qualitatively and quantitatively. At present, because of the lack of precision of initial and experimental data which has been pointed out, a more precise calculation of the rate constants of disproportionation reactions would be premature.

The ratio of the rate constants for the disproportionation and recombination of alkyl radicals can be calculated

from the results that have been obtained. Most of the experimental results (which have been discussed in detail by Stepukhovich[23] and Ulitskii[37]) are given in terms of Δ; experimental and calculated values can therefore be compared. As Table 2 shows, the theoretical ratios of the rate constants of radical disproportionation and recombination reactions are close to the corresponding experimental values.

A number of attempts have been made to correlate values of Δ with some characteristics of the processes under consideration. If such a correlation were established, known values of Δ for some reactions could be used approximately to evaluate the ratios of the rate constants for other reactions.

If, as Ausloos and Steacie assume[69], the rate constants for the recombination of different butyl radicals are equal, values of the ratio Δ will be proportional to the rate constants of the disproportionation reactions (k_2). Let $\Delta = ak_2$, the value of a being selected to make ak_2 equal to 5 for s-C_4H_9 radicals. The number of hydrogen atoms which could be eliminated from the radical to form an alkene product is indicated for comparison in the fourth column of Table 3. Clearly there is a similarity between the numbers in the third and fourth columns. This indicates (under conditions such that the rate constants of the recombination reactions are equal) that the main factor determining the rate of disproportionation of butyl radicals is the number of hydrogen atoms that could be eliminated from the radical to form a stable alkene.

Kerr and Trotman-Dickenson have shown[70] from experimental results that values of Δ(CH$_3$, Alk) are simply related to the analogous Δ(Alk, Alk) for the corresponding reaction of two identical alkyl radicals. They examined recombination and disproportionation reactions between the same and different radicals (CH_3, C_2H_5, iso-C_3H_7, and t-C_4H_9). The corresponding values of Δ(CH_3, Alk) and Δ(Alk, Alk) are shown in Table 4. The second column of this table shows the number of hydrogen atoms which can migrate in a disproportionation reaction in which CH_3 and Alk radicals participate; thus in a ethyl radical the number is 3, in an isopropyl radical 6, and in t-C_4H_9 it is 9 (the number is denoted by the symbol | H |). The fourth and sixth columns of Table 4 show what are termed reduced values of the ratios of the rate constants of radical disproportionation and recombination reactions (Δ/| H |). A linear relationship of the following type may be established for these values:

$$\log \frac{\Delta(CH_3, Alk)}{|H|} = 0.55 \log \frac{\Delta(Alk, Alk)}{|H|} - 0.95.$$

By means of this equation, known reduced ratios of the rate constants of reactions between the same radicals may be used to find analogous values for disproportionation and

TABLE 3. Ratio of the rate constants of disproportionation (k_2) and recombination (k_1) of butyl radicals near 100°C (it it assumed that k_1 is the same for all these reactions[69]).

Radical	k_2/k_1	$ak_2=2.2\frac{k_2}{k_1}$	| H |
t-C_4H_9	4.59	10.1	9
iso-C_4H_9	0.418	0.92	1
s-C_4H_9	2.27	5.0	5

TABLE 4. Ratio of the disproportionation and recombination rate constants of reactions between the same and different alkyl radicals[70].

Radical	| H |	Δ(CH$_3$, Alk)	$\frac{\Delta(CH_3, Alk)}{|H|}$	Δ(Alk, Alk)	$\frac{\Delta(Alk, Alk)}{|H|}$
C_2H_5	3	0.06	0.02	0.13	0.043
iso-C_3H_7	6	0.22	0.036	0.65	0.11
t-C_4H_9	9	0.70	0.078	4.6	0.51

recombination reactions between CH_3 radicals and other alkyl radicals. This relationship may be expressed in the more general form:

$$\log \frac{\Delta(Alk', Alk'')}{|H|} = 0.55 \log \frac{\Delta(Alk', Alk')}{|H|} + C,$$

which links the reduced rate constants of these reactions between like and unlike radicals (C is a constant which is equal to 0.95 when Alk = CH_3). Too much significance should not be attached to these linear relationships, since they are constructed from three experimental points¶. Moreover, the experimental results of Boddy and Robb[62] do not show such a correlation.

Obviously, correlations between values of Δ(Alk', Alk") and Δ(Alk', Alk') must link not only the number of hydrogen atoms that can migrate in radical disproportionation, but they must also include other characteristics of radical recombination and disproportionation. In particular, it has been found in a number of examples examined that changes in Δ(Alk', Alk") or Δ(Alk', Alk') and $S_{dis} - S_{rec}$ are symbathic and a relationship can be established between them[40]. Moreover, as Table 1 shows, there are no grounds for assuming that the reactivity of recombining radicals does not change with a change in their structure (this conclusion is true only for sufficiently complex radicals). Therefore, the assumption that the rate constants for the recombination of different radicals are equal is not always justified, and the assumption that the correlations depend only on radical disproportionation processes cannot always be considered valid.

The ratios of the rate constants for the disproportionation and recombination of alkyl radicals found in different experiments are close. The calculated values of analogous ratios of the rate constants agree with the experimental values (Table 5). Since the calculated and experimental values of steric factors of radical recombination reactions are low, and the ratios of the rate constants of reactions (1) and (2) are close to unity, the steric factors for the disproportionation of alkyl radicals are also low, and these determine the kinetics of the reactions.

Since it is concluded that the steric factors for the recombination and disproportionation of alkyl radicals are low, these reactions may be classified as fairly slow bimolecular reactions, and not as rapid bimolecular reactions (as has been done in the literature). At high temperatures (in the cracking of hydrocarbons and other thermal conversions) the steric factors are particularly low and the kinetics of the processes are determined entirely by these factors. Therefore, the not too high reaction

¶ With these relationships Δ(Alk', Alk") can be calculated from a knowledge of Δ(Alk', Alk') with an uncertainty covered by a factor of 3–4.[71]

TABLE 5. Calculated and experimental values of $\Delta = \frac{k_2}{k_1}$.

Reaction	Δ(theor.)	Δ(expt.)	Reaction	Δ(theor.)	Δ(expt.)
$H+C_2H_5$	0.29	—	$C_2H_7+C_3H_7$	0.16	$0.125^{66}0.16^{78}0.157^{79}$
$H+C_3H_7$	0.4	—	$C_2H_7+C_4H_9$	0.16	—
$H+C_4H_9$	0.53	—	$C_2H_7+C_6H_{11}$	0.16	—
$CH_3+C_2H_5$	0.08	$0.04^{69}\ 0.06^{72,73}$	$C_4H_9+C_4H_9$	0.17	$0.9^{80}0.57$—$1.04^{70}0.7^{41}$
$CH_3+C_3H_7$	0.08	$0.05^{74}\ 0.14^{75}$	$C_4H_9+C_6H_{11}$	0.19	—
$CH_3+C_4H_9$	0.17	0.15^{75}	$C_6H_{11}+C_6H_{11}$	0.2	0.2^{76}
$CH_3+C_6H_{11}$	0.17	0.1^{76}	2iso-C_3H_7	0.88	$0.6^{81,82}$
$C_2H_5+C_2H_5$	0.13	$0.14^{44,73,77}\ 0.15^{70}$	2iso-C_4H_9	0.43	$0.418^{80}0.165^{83}$
$C_2H_5+C_3H_7$	0.16	—	2s-C_4H_9	2.1	2.27^{80}
$C_2H_5+C_4H_9$	0.16	—	2t-C_4H_9	4.5	$4.59^{80}4.38^{84}3.2^{71}$
$C_2H_5+C_5H_{11}$	0.16	—			

rates of radical recombination and disproportionation reactions under these conditions are determined not only by the low radical concentrations in the reaction zone but also by low values of the preexponents.

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THE USE OF VIBRATIONAL SPECTRA IN THE STUDY OF THE STRUCTURE OF POLYATOMIC MOLECULES

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1. INTRODUCTION

One of the fundamental tasks in modern science is to study the structure and properties of polyatomic molecules. In the past two decades, in addition to traditional chemical methods, an ever-increasing and in many instances decisive part has begun to be played by various physical methods, particularly methods based on the study of the energy levels of polyatomic molecules. These methods include electronic, vibrational, and rotational spectroscopy and radiospectroscopic methods. The great importance of these methods lies primarily in the fact that they make possible the study of the structure and properties of molecules and molecular associates in any state of aggregation without breakdown of the molecules, as usually takes place when chemical methods are used. At present the methods most widely used are electronic and particularly vibrational spectroscopy. This is due both to the fact that historically they appeared before the radiospectroscopic methods and also to the high degree of development and ubiquity of electronic and vibrational spectroscopy and the wide range of varied problems which can be solved by these methods. The rapid development of experimental techniques and the appearance of automatic spectrophotometers have also been of considerable importance.

Unlike electronic absorption spectra and luminescence spectra, the overwhelming majority of vibrational spectra consist of a large number of discrete lines and bands, whose appearance is related to the presence and interaction of various atomic groups in the molecule, so that the very nature of the vibrational spectra gives considerable information on the detailed structure of a complex system.

Vibrational spectroscopy, however, is an indirect method. Experimental measurement of the parameters of the spectrum alone (the number of bands, their position on the frequency scale, intensities, etc.) is useless if a relationship has not been established between the observed quantities and the structure of the polyatomic molecule, that is, if the appropriate theory has not been developed. The need to develop a special theory of vibrational spectra arose in the nineteen-thirties and -forties as a result of the accumulation of experimental material on the infrared absorption spectra (IRS) and Raman spectra (RS) of complex molecules and the resulting desire to interpret these spectra. At that time a solution to the problem of the vibrational energy levels (normal vibrations) of polyatomic molecules had been roughly outlined; the problem involved primarily the development of a theory to explain the general features characteristic of the vibrational spectra of homologous series, to relate the vibrational spectra to the internal structure of molecules, and to carry out the necessary numerical calculations. This theory could be only semi-empirical, since direct quantum-mechanical methods were here quite inadequate.

A decisive step in this direction was taken by El'yashevich[1-6], who proposed a general method for formulating equations for the vibrations of polyatomic molecules in a special system of coordinates, which he called the natural system. An analogous method was developed independently by Wilson[7-10]. The introduction of natural coordinates made it possible to apply to the theory of vibra-

tional spectra the system of ideas developed in the structural chemistry of polyatomic molecules and this in turn made it possible to make the most important classification of all normal vibrations on the basis of the vibrations of the valency bonds (stretching vibrations), the vibrations of the valency angles (bending vibrations), and the vibrations of structural groups. This made it possible to explain the characteristic vibrations in the spectra of homologous theories. The theory of characteristic vibrations was later developed by Mayants [11] on the basis of a classification of the vibrations according to the characteristic nature of the frequency and mode, and also the frequency and mode themselves.

When natural coordinates were used, the coefficients in the expression for the potential energy (force constants) in a large number of molecules were found to be closely related to the properties of the corresponding structural elements, and specific calculations showed that the force-constant structural elements, within certain limits, retain their numerical value in a series of molecules containing the given structural elements. This property of the force constants, which is closely related to the comparatively unchanged nature of the individual "building bricks" of the molecule, predetermined the collection of a set of force constants necessary for numerical calculation of the vibration frequencies of a large number of molecules.

The creation of this set began after the development of effective methods for calculating the eigenvalues and eigenvectors of the equations for molecular vibrations, taking account of the specific features of these equations (the diagonalisation method of El'yashevich and Stepanov [12], the improved iteration method of Mayants [13]), and the determination of the force constants for a number of basic compounds by Stepanov and El'yashevich [14]. On the basis of the theory developed by these authors, Kovner's and Sverdlov's groups, together with Kovalev, Bogomolov, Peregudov, Popov, and a number of others, calculated the frequencies and modes of the vibrations and interpreted a large number of molecular spectra (chiefly organic molecules) and determined the force constants of the most important bonds and groups. This provided the necessary starting material for the extensive use of calculations and the solution of a variety of applied problems.

The development of the theory of molecular vibration frequencies was accompanied by the development of a theory of intensities in IRS and RS. By using an additive scheme for representing the dipole moment and polarizability tensor of a molecule in the form of the vector and tensor sums of the dipole moments and polarizability tensors of the individual bonds, Vol'kenshtein [15,16] formulated a semi-empirical theory of intensities in IRS and RS, later improved with El'yashevich [17,18]. Because of the lack of experimental material on the measurement of intensities in spectra at that time and the tedious nature of the calculation, however, the theory of intensities remained at this stage of development for a prolonged period.

Thus at the start of the nineteen-sixties considerable progress had been made in the theory of vibrational spectra (particularly in the theory of the frequencies and modes of the vibrations), as a result of which the extensive application of calculation methods to practical spectrochemical studies became possible. It was also shown for many examples that in the overwhelming majority of instances sufficiently well-founded and reliable conclusions regarding the structure and properties of a molecule could be obtained from spectroscopic data only by a theoretical study.

This possibility, however, could not be completely realised until all the calculation part had actually been reduced to programmes for electronic computers (EC). This important task in turn required the transformation of the entire mathematical technique of the theory into a form convenient for use with EC, and the development of a system of algorithms. EC were first used to calculate the eigenvalues and eigenvectors of the equations for the vibrations, and also for a number of other operations (normalisation, calculation of the displacements of atoms, etc.) [19]. This is related to the fact that the methods for solving the equations are already formulated in the form of algorithms and the problem involves merely encoding.

The choice of algorithm for formulating the equations, which is the specific task of the theory of molecular vibrations, was found to be much more complex. It is significant that programmes of this type have appeared only recently [20]. The solution of this problem required not only a change in the mathematical techniques but also the abandonment of most of the procedures used in manual calculation. For example, the use of standard formulae for calculating the kinematic coefficients was found to be unsuitable.

The reduction of the mathematical apparatus of the theory to a single form and its simplification inevitably concerned one of the most important sections of the theory — the consideration of the symmetry of the molecule and the calculation of the symmetry coefficients in the symmetry coordinates. All the other sections of the theory of molecular vibrations can be readily formulated in the language of vector and matrix algebra and require for their understanding a fairly limited knowledge of these branches of mathematics, but the calculation of the symmetry coefficients was based on the use of group theory, unfamiliar to the great majority of spectroscopist chemists. Despite the existence of tables of symmetry coefficients, this feature created serious difficulties in carrying out the calculations for specific molecules. The attempt by Mayants [21] to solve this problem without using group theory was thus understandable, but the method which he proposed was also tedious and was not widely accepted. A simple solution to this problem and clear selection rules depending on symmetry in the IRS were obtained only recently by introducing the concept of directed symmetry vectors and the study of their properties [22].

A most important problem, unfortunately still unsolved, is that of decreasing the arbitrary nature of the choice of force constants for polyatomic molecules. The existing modifications of the force functions have not led to a cardinal solution and cannot be regarded as satisfactory. Since direct application of the methods of quantum mechanics to the solution of this problem is still impossible, the development of the theory of molecular vibrations must apparently involve the construction of a theory which will also require the use of empirical parameters whose introduction, however, will be based on the results of quantum chemistry. The ordinary force constants should then be functions of these parameters.

In recent years the theory of intensities in the IRS has been further developed. As noted above, the work of Vol'kenshtein and El'yashevich, who laid the foundations of the theory, was followed by stagnation for several years. In this period the non-Soviet literature included a large number of papers (see the bibliography in the review by Gribov and Smirnov [23]) on the measurement of the absolute intensities of absorption bands in the IRS using methods

developed by Kemble and Bourgin[24,25], Wilson and Wells[26], and others[27]. On this basis attempts were made to calculate the dipole moments of the bonds in many molecules. The failure of these calculations (the lack of agreement between the dipole moments of the molecules determined by other methods and the values calculated from the IRS) produced a sceptical attitude towards the theory itself. Sverdlov's calculations[28-32] of the electro-optical parameters of a number of simple molecules, carried out from 1959 onwards according to the scheme of Vol'kenshtein and El'yashevich, did not greatly improve the situation, since the parameters which he found were obtained in the form of combinations which were so cumbersome that their physical significance was completely lost and their further use impossible.

Thus the theory of intensities was faced with the following tasks: the extension of the theory to any molecules (additive and non-additive), the creation of a convenient calculation scheme, the development of some of the most important general questions (the theory of characteristic intensities and the dependence of the intensities on the number of identical groups in the molecule) formulated in Vol'kenshtein's papers, determination of the numerical values of the electro-optical parameters for a number of the simplest groups, and proof that the values for these parameters are preserved in a series of molecules containing the given groups. This last problem determined the possibility of creating a set of electro-optical parameters for bonds and groups, similar to the set of force constants, and hence the possibility of using the theory to carry out numerical calculations of the absorption band intensities in the IRS. A number of papers by the authors of the present review were devoted to the solution of all these problems[33-43]. As a result it was possible for the first time to calculate the intensities of the absorption bands in the spectra of complex molecules[42,43]. In recent papers[44-46], the methods of the theory of intensities in the IRS are used to study the structure and properties of a number of compounds. It can thus now be stated that the theory which has been developed can serve as a basis for corresponding spectrochemical studies.

More work has also been carried out on the theoretical study of the electro-optical parameters for Raman spectra using a modernised form of Vol'kenshtein's calculation scheme[47-51], but the existing situation (the number of empirical parameters introduced is three times that for IRS) does not lead us to expect marked advances in this direction.

Methods for analysing molecules according to their vibrational spectra can be provisionally divided into two groups according to the nature of the problems to be solved. The first group includes methods which use only directly measurable quantities (the number of absorption bands or lines in the RS, their position on the frequency scale, and their intensities). These data make it possible to determine the symmetry of molecules and free radicals, to calculate thermodynamic functions, and to carry out qualitative and quantitative molecular analysis and the analysis of mixtures.

The second group includes methods of structural group analysis, the isolation of atomic groups with closed structure in the molecule, the study of the influence of the environment of the group, substituents, intramolecular interaction, and intermolecular interaction, and the study of rotational isomers. In these studies, in addition to the measured parameters of the spectrum, it is necessary to have additional information on the relative amplitudes of the vibrations of the parts of the molecule in a given normal vibration (the mode of the vibration), and also on those factors (the geometry of the molecule, the characteristics of the interatomic forces and interactions between the groups, the dipole moments of the bonds, etc.) which determine the position of the bands or lines in the spectrum, and their intensity and polarisation (or depolarisation). The accumulation of information of this type is generally described as the interpretation of the band (or line). A sufficiently reliable and complete interpretation of a band can be obtained only on the basis of appropriate theoretical study and model calculations.

In studies of the first type, a close combination of theoretical and experimental methods is often necessary. For example, in the calculation of the thermodynamic functions of polyatomic molecules (free energy, entropy, heat capacity), calculation makes it possible to find all the vibration frequencies, which cannot always be done by purely experimental methods, and also to distinguish, among the observed bands or lines, those due to the fundamental frequencies.

At the present time, when it is constantly necessary in chemistry to use the results of spectroscopic studies, it is absolutely essential for chemists not only to be aware of the fundamental possibilities and characteristic features of the method, in general outline at the very least, but also to be familiar with the "pitfalls" characteristic of this method. Otherwise, it is impossible to adopt a critical attitude towards published material, and this may have very serious consequences. Unfortunately, it must be said that although the method of vibrational spectroscopy has for long been fruitfully used in chemical studies, a very large number of chemists, even sometimes those who make fairly extensive use of the infrared spectra and Raman spectra of polyatomic molecules, have insufficiently clear ideas regarding the most important aspects and concepts of the method. This situation has apparently arisen as a result of the fact that existing publications on the problems of vibrational spectroscopy can be fairly sharply divided into theoretical publications intended for specialists in this field and, if we can use the expression, experimental publications based chiefly on various types of empirical studies of individual classes of compound. The latter often contain very valuable material but their perusal gives an oversimplified and often incorrect picture of the methodology of vibrational spectroscopy.

It is of course impossible in a single paper to outline even briefly the essential features of the many important and interesting problems of vibrational spectroscopy. We shall therefore restrict ourselves to two of the most important: the influence of kinematics on the position of the frequencies in the spectrum, and its consequences, and also the problem of determining force constants. It is these two problems which arise most frequently in spectrochemical practice, and without a clear understanding of these problems any serious spectroscopic study of the structure and properties of polyatomic molecules is impossible. Most errors in spectrochemical work, moreover, are due to neglect of kinematic factors.

2. ELEMENTS OF THE THEORY OF VIBRATIONS OF POLYATOMIC MOLECULES

The appearance of the discrete vibrational spectrum of a polyatomic molecule results from the existence of definite

energy levels in the molecule. Of fundamental importance in the discussion of the problems of energy levels in polyatomic molecules is the possibility of examining separately, with a reasonable degree of approximation, the various forms of motion for the particles in the molecule: the motion of electrons, vibration of nuclei, rotational motion of the molecule as a whole, and finally the translational motion of the molecule.

We shall be interested in the purely vibrational motion, that is, the movement of the atoms in a force field which is determined by the given electronic state of the molecule. The equations of motion are usually formulated in the system of natural vibrational coordinates q_i (the changes in the equilibrium bond lengths, valency angles, etc.), the number of which is equal to the number of vibrational degrees of freedom for a system of N particles, that is, $3N$ - 6 (or $3N$ - 5 for linear molecules)†.

The coordinates q_i, which characterise the departure of the configuration of the molecule from the equilibrium configuration and become equal to zero for the equilibrium state, describe the state of the separate parts of the molecule. For small vibrations (of the order of hundredths of an ångström unit) they are linearly related to the Cartesian coordinates of the displacement of the atoms from their equilibrium positions, so that the kinetic energy of the vibrating atoms is described in the generalised momenta p_i corresponding to the coordinates q_i in the quadratic form

$$T_{\text{kin}} = \frac{1}{2}\sum_{i,j} \tau_{ij}\, p_i p_j,$$

with coefficients τ_{ij}, which can be calculated if the equilibrium geometry configuration of the system is known. The potential energy, which has the significance of the difference between the energies of the displaced and equilibrium configurations, depends only on the relative coordinates of the nuclei to a reasonable degree of approximation and is described by the function $V(q)$. By expanding $V(q)$ into a series with respect to powers of q_i close to the equilibrium position, it is possible to represent the potential energy of any displaced state by means of a set of derivatives of $V(q)$ with respect to q_i of different order and a set of values of q_i. These derivatives are constant for any small deformations of the molecule and are determined by the properties of the given electronic state. It is assumed (in the so-called harmonic approximation which is satisfactory for small vibrations) that the displacements of the atoms from the equilibrium positions during the vibrations are symmetrical and that the resulting restoring forces are linearly dependent on the magnitude of the displacement. We then have (with allowance for the conditions of stable equilibrium)

$$V = \frac{1}{2}\sum_{i,j} K_{ij} q_i q_j$$

The coefficients $K_{ij} = \left(\dfrac{\partial^2 V}{\partial q_i\, \partial q_j}\right)_0$ (the force constants) are at present found only from measurements of the vibrational frequencies of the molecule. This feature, which makes the theory of vibrations semi-empirical, is its chief weakness, since it restricts the possible applications of the theory in calculations chiefly to organic molecules. In order to solve the equation for the vibrations it is necessary to change to new coordinates, which have been called normal coordinates. When normal coordinates are used the expressions for the kinetic and potential energies acquire the form $T_{\text{kin}} = \frac{1}{2}\sum_i P_i^2$ and $V = \frac{1}{2}\sum_i \lambda_i Q_i^2$, that is, they do not contain the terms P_iP_j and Q_iQ_j $(i \neq j)$. This can be achieved by the following change of variables (coordinates)

$$q_1 = l_{11}Q_1 + l_{12}Q_2 + \ldots + l_{1n}Q_n,$$
$$\ldots\ldots\ldots\ldots\ldots\ldots$$
$$q_n = l_{n1}Q_1 + l_{n2}Q_2 + \ldots + l_{nn}Q_n \quad (n = 3N - 6).$$

The coefficients λ_i and elements l_{ij} are found from the solution for the system of $3N$ - 6 algebraic equations:

$$\begin{cases} (d_{11} - \lambda)q_1 + d_{12}q_2 + \ldots + d_{1n}q_n = 0 \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ d_{n1}q_1 + d_{n2}q_2 + \ldots + (d_{nn} - \lambda)q_n = 0 \end{cases} \quad (1)$$

where $d_{ij} = \sum_m \tau_{im}K_{mj}$.

This system of equations assumes a non-trivial solution for q_i only for certain values of the factor λ, which are calculated from the condition for solvability of the system; this makes it possible to formulate an equation of degree $3N$ - 6 in λ (the secular equation). For each root λ_i with subscript i for this equation we find from system (1) a set of unknowns $q_1 \ldots q_n$, whose value is given by the elements l_{ki} $(k = 1, \ldots, n)$ in the formulae for the transformation of the coordinates.

After the change to normal coordinates, the equation for the vibrations is broken down into $3N$ - 6 first-order equations, each of which describes a linear harmonic oscillator and can be readily solved. The frequencies of the vibrations of these oscillators (normal vibrations) will be equal to $\nu_i = \sqrt{\lambda_i}$. To characterise the vibrations of the individual parts of the molecule, it is necessary to change again from coordinates Q_i to natural coordinates. In each normal vibration, only one coordinate Q_i will be different from zero. We then have, for example, for the first coordinate according to the formulae for transformation of the coordinates,

$$q_1 = l_{11}Q_1,\ q_2 = l_{21}Q_1,\ \ldots,\ q_n = l_{n1}Q_1. \quad (2)$$

Thus the relative amplitudes of the changes in all the natural coordinates in the vibrations will be given by the numbers l_{k_1}, and the relative phases will be determined by the signs of l_{k_1}. The set of elements l_{k_1} is therefore called the mode of the given normal vibration. It can also be seen that the changes in all q_i in a normal vibration will take place with frequency ν_i and that all q_i pass through zero simultaneously.

Despite its limitations (the harmonic approximation), the concept of normal vibrations is important in the theory of the vibrations of polyatomic molecules and provides a basis for solving the most varied problems.

3. CHARACTERISTIC VIBRATIONS OF POLYATOMIC MOLECULES

Study of the properties of normal vibrations makes it possible to reach general conclusions regarding the behaviour of the vibrational frequencies in the spectra on

† Strictly speaking, the coordinates used are the projections of these changes on the equilibrium unit vectors of the molecule (the directing vectors of the bonds, valency angles, etc.), which undergo translational movement and rotate with the molecule.

going from a given atomic group in one molecule to the same group in another molecule. This problem is important in applied spectroscopy, since the great majority of present-day spectrochemical investigations are aimed at studying the influence exerted on a given group of atoms by its immediate environment and in some instances by its more distant environment. Measurements are usually made of the displacements of the vibration frequencies for the given group with change in its environment. The magnitude of these displacements and the observed regular features in a series of compounds contain information on the structure and properties of the group itself and on the changes in the structure of the molecule. This obviously raises a most important question — does the displacement or change in the intensity of the absorption bands characteristic of a given group provide a sufficient indication of breakdown of its structure? It is known, for example, that this is in fact the case for the electronic absorption spectra of polyatomic molecules. This feature, and also the fact that some experimental workers are insufficiently familiar with the general theory of the vibrations of polyatomic molecules, leads to a situation where the authors of whole series of papers tend to interpret any change in the position or intensities of the vibrational absorption bands in the IRS or lines in the RS due to a given group as a sign of breakdown in the structure of the group; they forget long-familiar simple experimental facts which show directly that appreciable displacements of the frequencies may have no connection with breakdown of the electronic structure of the molecule. For example, the frequency of the vibrations of the C≡C bond is extremely stable in various compounds but changes from 1974 cm^{-1} in the acetylene molecule to 1851 cm^{-1} in monodeuterioacetylene and to 1765 cm^{-1} in dideuterioacetylene, that is, by a total of more than 200 cm^{-1}, although it may be assumed with a reasonable degree of approximation that no changes in the properties of the electronic ground state of the molecule take place when H is replaced by D.

It is quite obvious that without a clear understanding and detailed study of all the factors leading to change in the bands studied in the spectrum, no reliable conclusions can be reached regarding changes in the molecule.

Here we come up against the most important concept of characteristic vibrations. The existence of characteristic vibrations has to a large extent been responsible for the extensive application of vibrational spectroscopy in spectrochemical practice. At the same time no topic has been associated with so many errors as the interpretation of characteristic vibrations‡. To examine the essential features, let us take a simple example.

Let us imagine a given group of atoms. Let us assume that this group is present in a molecule. Since each vibration of the molecule is characterised by its frequency and mode, it is natural to classify vibrations according to their frequencies and modes [52]. When the frequencies of vibrations are measured, their mode is not recorded directly, but it is of decisive importance in the study of the intensities of vibrations. There may be vibrations which are stable with respect to frequency but not with respect to mode, so that the absorption bands in the IRS and lines in the RS retain their position in the spectrum, but with a change in intensity.

‡ It is paradoxical that in this an undesirable part has been played by various tables of characteristic vibrations, which in many cases are accepted too literally.

We shall describe a vibration as characteristic with respect to frequency for a given group if one of the normal vibrations of the molecule coincides in frequency with one of thenormal vibrations of the given group as a free molecule. If one of the normal vibrations of the molecule coincides with a normal vibration of the given group with respect to mode, that is, if the vibration is such that only the configuration of the isolated group changes, this vibration will be described as characteristic with respect to mode for the given group. If both conditions are satisfied, the vibration will be described as characteristic with respect to frequency and mode or completely characteristic. This distinction is meaningful (although strictly speaking there cannot be vibrations characteristic with respect to frequency but not characteristic with respect to mode, and vice versa), because the degree of non-characteristic nature of different types is different in a very large number of instances. This classification is to some extent arbitrary and approximate, but it has nevertheless been found to be extremely convenient in practice.

There may be instances where the above properties of normal vibrations are preserved in a series of molecules containing a given group. It is then usual to speak of the stable characteristic nature with respect to frequency, mode, and frequency and mode for a given group. The property of stability in characteristic nature with respect to frequency and with respect to frequency and mode is manifested by the appearance of absorption bands or lines in the same region of the IRS for a series of molecules containing the given group. This in turn makes it possible to carry out the qualitative analysis of unknown substances and mixtures from their IRS and RS and their structural group analysis.

Let us consider the basic hypotheses of the theory of characteristic vibrations. For this purpose let us examine a given group of atoms (radical) and let us introduce it in turn into different molecules of a given series, that is, let us examine a set of molecules consisting of two groups (first and second), where the first group remains unchanged. It is obvious that in these molecules we can expect the appearance of characteristically normal vibrations only if the contribution made by the group being studied is additive. It is also clear that the distortions of the normal vibrations of the selected group as a free group when it is attached to a molecule will be smallest when the group is attached to the molecule through a single atom. We shall therefore restrict ourselves to the case where the group has only one atom attached to the molecule.

Let us divide the natural coordinates characterising the vibrations of molecules into three sets: coordinates describing the movement of the first and second groups as free molecules (natural vibrations of the groups), and coordinates describing the movements of the first and second group relative to one another. If the first and second groups are assumed to be additive, with a reasonable degree of approximation, the expression for the potential energy need take account only of the coefficients K_{ij} (force constants), relating to the internal coordinates of the first and second groups and intermediate coordinates. Here the force constants of the groups will depend only on the properties of these groups taken separately. In the formulation and solution of the equations for the vibrations of the first and second groups as free molecules and the equation for the vibration of these groups relative to one another, we can change from natural coordinates to normal coordinates for each of the groups. This form of representation is convenient in the investigation of the nature of

the characteristic vibrations, since it makes it possible to describe the normal vibration of a molecule as the superposition of the normal vibrations of the individual groups. It should be remembered that the change to normal coordinates can be regarded as the construction of a molecular model in which the real system is replaced by a set of one-dimensional oscillators — bonds — selected in definite fashion. When two groups are combined to form a single molecule the various normal oscillators of the first and second groups will interact with one another and the resulting vibration will be complex. In order to analyse the qualitative picture we can restrict ourselves to the instance where only pairs of normal oscillators of the first and second groups interact, that is, to the interaction of pairs of hypothetical "bonds".

The equation for the vibrations of this pair of "bonds" will have the form

$$\begin{cases}(\lambda_1^{(0)}-\lambda)Q_1+\tau\lambda_2^{(0)}Q_2=0,\\ \tau\lambda_1^{(0)}Q_1+(\lambda_2^{(0)}-\lambda)Q_2=0,\end{cases} \quad (3)$$

where $\lambda_1^{(0)}$ and $\lambda_2^{(0)}$ are the squares of the frequencies of the selected pair of normal vibrations of the first and second groups (these frequencies are usually called partial frequencies), and Q_1 and Q_2 the corresponding normal coordinates, which have the physical significance of the "elongation" of the hypothetical "bonds". The quantity τ (the coefficient of kinematic interaction of the pair of oscillators) is inversely proportional to the mass of the atom which is common to both groups and to the cosine of the angle α between the "directions" of the normal oscillators.

When the common atom has a high mobility and the angle α approaches 180°, the value of τ may become appreciable. It then follows from Eqn. (3) that the normal vibrations of the pair of "bonds" will not have frequencies equal to $\lambda_1^{(0)}$ and $\lambda_2^{(0)}$ and modes $Q_1 = 1$, $Q_2 = 0$ and $Q_1 = 0$, $Q_2 = 1$ respectively, that is, they will not be characteristic either with respect to frequency or with respect to mode for each of the "bonds". We thus reach an extremely important conclusion: the vibrations of a group of atoms may change both with respect to frequency and with respect to mode in a series of molecules containing the given group merely as a result of its kinematic associations with the rest of the molecule, even if the structure of the group itself remains quite unchanged. Thus the displacement of absorption bands assigned to a given group of atoms, or a change in their intensity (the latter depends very strongly on the mode of the vibrations) for different types of substitution outside the given group cannot provide a sufficient indication for breakdown of the structure of the group. On the other hand, absence of change in the frequency, and more particularly, the intensity of a band in the IRS or of a line in the RS indicates with a very high degree of probability that the group itself remains unchanged.

Despite its obvious nature, this feature has somehow been overlooked in many papers. It is sufficient to point out that errors of this type are not infrequent in Bellamy's well-known monograph[53], a handbook of the majority of spectrochemists. Displacements of frequencies as a result of kinematic associations are particularly large for groups situated inside a molecule but they may reach 100 cm^{-1} or more even for terminal groups. A classical example of this type is the marked displacement of the bands and changes in their intensities on deuteration, which often leads to a change in frequencies corresponding to the vibrations of groups in which no replacement of H by D has taken place.

The possibility of appreciable displacements of absorption bands or lines in the IRS as a result of kinematic interaction is responsible for fundamental difficulties in the study of molecules by the methods of vibrational spectroscopy. In order to make allowance for kinematic factors it is almost always necessary to calculate the frequencies and modes of vibrations for the selected molecular models. It is most convenient to begin with calculations for simplified models and then to proceed to more complicated structures as required.

Let us assumed that the atom by means of which the group is attached to the molecule is much heavier than the other atoms. It will then undergo almost no displacement when the group vibrates. It is obvious that then we shall be dealing with vibrations which are characteristic with respect to frequency and mode for the given group. In actual fact this corresponds to the case where $\tau = 0$. This property is shown, for example, by the vibrations of CH, OH, NH, CH_2, CH_3, NH_2, and other groups containing a light terminal atom.

For most groups $\tau \neq 0$. Of practical interest in this connection are the two extreme cases: $\lambda_1^{(0)} = \lambda_2^{(0)} = \lambda$ and $\lambda_1^{(0)} \gg \lambda_2^{(0)}$ $(\lambda_1^{(0)} \ll \lambda_2^{(0)})$.

Let us assume that $\lambda_1^{(0)} = \lambda_2^{(0)} = \lambda^{(0)}$; by solving Eqn. (3) we find that the kinematic interaction of the corresponding pair of normal vibrations of the first and second groups leads to the production of two vibrations, for which the squares of the vibrations are $\lambda_{1,2} = \lambda^{(0)} \pm \tau\lambda^{(0)}$ and the relative amplitudes (modes) are $Q_1^{(1)} = 1$, $Q_2^{(1)} = 1$, $Q_1^{(2)} = 1$, and $Q_2^{(2)} = -1$.

Thus the interaction of two normal vibrations of groups with identical frequencies leads to splitting of the frequencies and "mixing" of the amplitudes. This is one example of mechanical resonance. For its production, the natural vibrations of the first and second groups must contain vibrations with identical frequencies, and the displacement of the common atom in these vibrations of the first group should differ from zero and should not take place in a direction perpendicular to the displacements in the resonating vibration of the same atom of the second group. When resonance takes place the vibration of the first group extends throughout the entire molecule and will not be characteristic for this group either with respect to frequency or with respect to mode. The phenomenon of mechanical resonance is observed particularly frequently in the vibrations of molecular skeletons, so that they are almost never characteristic for individual bonds. This can readily be seen, for example, from Table 1, which gives the calculated modes of vibrations of the polyene chain in the $C_2H_5OOC[CH=CH]_4COOC_2H_5$ molecule.

If $\lambda_1^{(0)} \gg \lambda_2^{(0)}$, we obtain vibrations for which the squares of the frequencies are equal to

$$\lambda_1 \simeq \lambda_1^{(0)} + \frac{\tau^2\lambda_1^{(0)}\lambda_2^{(0)}}{\lambda_1^{(0)}-\lambda_2^{(0)}};\quad \lambda_2 \simeq \lambda_2^{(0)} - \frac{\tau^2\lambda_1^{(0)}\lambda_2^{(0)}}{\lambda_1^{(0)}-\lambda_2^{(0)}}$$

and the relative amplitudes are

$$Q_1^{(1)} = 1;\ Q_2^{(1)} = \frac{\tau\lambda_1^{(0)}}{\lambda_1^{(0)}-\lambda_2^{(0)}} \to \tau \neq 0,$$

$$Q_1^{(2)} = \frac{-\tau\lambda_2^{(0)}}{\lambda_1^{(0)}-\lambda_2^{(0)}} \to 0;\ Q_2^{(2)} = 1.$$

TABLE 1*. Mode of the vibrations of the polyene chain in $C_2H_5OOC(CH=CH)_4COOC_2H_5$.

Symmetry	ν, cm^{-1}	Mode of the vibration			
		Q	q	Q_1	q_1
A_g	1623	—0.28	0.05	0.27	—0.24
	1597	0.25	—0.31	0.26	—0.18
A_u	1626	0.15	—0.30	0.35	—
	1573	—0.36	0.10	0.19	—

* Q and q are the normalised modes of the vibrations in symmetry coordinates, characterising the changes in the lengths of the double and single bonds respectively (from the start of the chain to the centre).

Thus both frequencies will differ from the natural frequencies of the vibrations of the first and second groups, and if the natural frequency of the first group is greater than the natural frequency of the second group, its vibration will extend throughout the whole molecule with coefficient τ. If $\lambda_1^{(0)} \gg \lambda_2^{(0)}$, the relative displacement of the λ_1 relative to $\lambda_1^{(0)}$ will be small and we can speak of the production of vibrations characteristic for the first group with respect to frequency but not with respect to mode. This property is shown, in particular, by the stretching vibrations of non-conjugated C=C, C≡C, N=N, and certain other bonds. For example, in the ethylene molecule for the 1620 cm^{-1} vibration the extension of the C=C bond is accompanied by a marked change (of up to 50% in arbitrary units) in the HCC angles. In the stretching vibration with frequency 2270 cm^{-1} in the acetonitrile molecule, usually assigned to the vibration of the C≡N bond, a significant part is played by the neighbouring C–C bond (up to 50%). Neglect of this feature has led, in particular, to an incorrect explanation[54] for the almost eightfold change in the intensity of this absorption band when hydrogen atoms are replaced by chlorine[45].

The second normal vibration of the set of coupled oscillators when kinematic interaction takes place will have a frequency less than $\lambda_2^{(0)}$ (for $\tau > 0$), but it does not extend throughout the whole molecule. There appear vibrations which are not characteristic with respect to frequency for the first group but are characteristic with respect to mode.

Let us take one simple example (the HCN molecule) which effectively illustrates the case of the interaction of the vibrations of two groups described above. Since the C atom is much heavier than the H atom, the H–C vibration will be characteristic with respect to frequency and mode. Accurate calculation[39] gives $\nu_1 = 3312$ cm^{-1} and $q_1 = 1$ (stretching of the C–H bond) and $q_2 = -0.136$ (stretching of the C≡N bond). The frequency of the vibrations of the C≡N bond is lower than the frequency of the vibrations of the C–H bond, so that in the C≡N vibrations the change in the length of the C–H bond should be less than the change in the C≡N bond. We have $\nu_2 = 2089$ cm^{-1}, $q_1 = 0.37$, and $q_2 = 1$. When H is replaced by D for C≡N vibrations the decrease in the D–C frequency relative to the H–C frequency makes possible resonance of the D–C and C≡N vibrations. We have in fact: $\nu_1 = 1921$ cm^{-1}, $q_1 = 1.13$, and $q_2 = 1$. "Mixing" of the vibrations takes place. This case of resonance and in general change in the mode of the vibrations is found very frequently in deuteration, so that, as already noted, deuteration is often accompanied not only by displacement of many absorption bands in the spectrum but also by an extremely sharp change in their intensities. This may even introduce difficulties in the interpretation of the bands. A good example of this is provided by the acetonitrile molecule[44]. Its spectrum shows vibrations with frequencies of 919 cm^{-1} and 1059 cm^{-1}, which may be interpreted as the stretching vibration of the C–C bond and external bending vibrations of the HCC angles. It might seem that this interpretation can be readily verified by deuteration. When this is done we obtain two frequencies at 850 cm^{-1} and 833 cm^{-1}, that is, both of the controversial bands are displaced by a considerable amount. This is again due to resonance of the vibrations.

To summarise, we can reach a number of conclusions regarding the possibility of existence of vibrations characteristic of a given group. These conclusions are qualitative in character, but they may help, in a large number of instances, to achieve rapid orientation in a spectrum and evaluation of various phenomena, and also to select the analytical absorption bands necessary for solving appropriate specific problems. They can of course be used only to explain sufficiently marked effects.

1. If the atoms of the first group, shared with another part of the molecule, are much heavier than all the other atoms of this group, we should observe vibrations which are characteristic with respect to frequency and with respect to mode for the given group. The position of the band in the spectrum and its intensity (if the group is additive and if certain other conditions are satisfied)[33] will be determined only by the parameters of this group. When these conditions are satisfied in a series of molecules we shall observe absorption bands whose frequency and intensity are preserved. With substitution of any groups in the molecule, the displacements of the bands of the group being studied and the changes in their intensity will be associated with breakdown of its structure.

2. A vibration will also be characteristic with respect to frequency and with respect to mode when in a given normal vibration the set of atoms shared with the remainder of the molecule does not undergo displacement or when this displacement takes place perpendicular to the displacements of these atoms for all normal vibrations of the remainder of the molecule. The frequency and mode of this vibration is again determined chiefly by the properties of the given group, but they will now be more sensitive to the environment, since replacement of atoms outside the group may lead to breakdown of the above condition that the movements of the common atoms in the normal vibrations of the first and second groups be at right angles to one another.

3. If any of the normal frequencies of the selected group and one of the normal vibrations of the remainder of the molecule coincide and the common atoms in these vibrations do not move in mutually perpendicular directions, resonance between the vibrations of these two groups is possible. We then obtain two normal vibrations of the entire molecule, whose frequencies and modes will not coincide with the frequencies and modes of the component vibrations, that is, the vibration will not be characteristic with respect to frequency and mode, in particular for the first group. The position and intensity of the corresponding band in the spectrum will be determined by the properties of the entire molecule and will change with substitution outside the group being studied. As already noted, the various skeletal vibrations of organic molecules are extremely common examples of such vibrations.

4. If the frequencies of the normal vibrations of a given group are greater than the frequencies of the normal vibrations of the adjoining part of molecule and if the common atoms are mobile in the vibrations, we may observe vibrations which are characteristic with respect to frequency for the group being examined but which are not characteristic with respect to mode. The position of the corresponding bands in the IRS or of lines in the RS will be determined by the properties of this group, and their intensities will depend on the properties of the environment (they will sometimes even be determined entirely by the properties of the environment[33]). With substitution outside the group being examined, the frequencies of its vibrations may remain unchanged, but the intensities must alter. An example of such vibrations is provided by the previously mentioned stretching vibrations of the C≡N bond in the molecules of acetonitrile and trichloroacetonitrile. The frequencies of the C≡N vibrations in these molecules are extremely close (2267 cm^{-1} and 2256 cm^{-1} respectively), but the intensities of the absorption bands differ appreciably.

5. If the frequencies of the normal vibrations of the group being considered are lower than the frequencies of the normal vibrations of the surrounding groups, vibrations may be produced which are characteristic with respect to mode for the given group but which are not characteristic with respect to frequency. As an example we can take the bending vibrations of the C–C≡N group in the CH_3CN and CCl_3CN molecules. These vibrations show an appreciable difference in frequency (380 cm^{-1} and 160 cm^{-1} respectively) but have almost identical modes[44,45].

All our discussion has concerned the instance where the groups are additive, that is, where there is no mutual electronic influence. We have seen that, even with this condition, it is only as a result of purely mechanical factors that the absorption bands or lines observed in the IRS can undergo appreciable displacement and change in intensity. For real molecules this treatment is often too approximate, and the displacements of the absorption bands observed in practice for various types of substitution result from a large number of factors.

In recent years a large number of papers have given correlations, for many functional groups, between the vibration frequencies (and in a number of instances, the intensities) and the electronegativities of the substituents, the Hammett constant σ, the Taft constant, etc. The search for various types of correlation can only be welcomed, but it must be remembered that, as shown by the above discussion, the reduction of the large number of factors determining the value of the vibration frequencies, even of the characteristic vibrations for an individual group, to a single factor cannot in general be justified. In particular, such correlations are meaningful only when the influence of kinematics is taken into account or is known to be small. Unfortunately, this last feature is not always recognised, so that in a number of instances the relationships obtained have no physical significance.

The chief requirement for the correct utilisation of spectroscopic data is an estimate (as far as possible quantitative) of the influence of various parameters on the position and intensity of the frequencies. This is tedious but it is the only way. A basis for such studies may be provided by the existing theory of the vibrations of polyatomic molecules; despite a number of inadequacies, this theory is quite capable of solving a large number of very important general and specialised problems.

The simplest is the determination, on the basis of the assumed symmetry of the molecule, of the number of fundamental vibrations which will be shown in the infrared and Raman spectra. Comparison of the calculated total number of vibrational frequencies active in a given spectrum, or of only that fraction of the vibrations which should be observed in a narrow range of the spectrum, with the experimentally-observed number of frequencies often makes it possible to establish unambiguously the symmetry of the molecule being studied. This method has for long been widely applied in the study of the structure of molecules, particularly in the gaseous phase. For example, the absence from the infrared spectrum of frequencies observed in the Raman spectrum, and vice versa (mutual exclusion) indicates unambiguously the presence of a centre of symmetry. In particular, the use of the mutual exclusion rule often makes it possible to identify reliably the structure of *cis*- and *trans*-derivatives of ethylene and diene compounds with identical substituents.

By solving the equation for the vibrations for the example where a set of force constants is known even provisionally, it is possible to calculate all the vibration frequencies of the molecule. The importance of this even approximate calculation is that it makes it possible to find the frequencies of vibrations which are not revealed either in the absorption spectrum or in the Raman spectrum. Moreover, not all the frequencies of the vibrations can be determined experimentally because of the low intensity of the corresponding lines and bands or because of the absence of suitable instruments (for example, for measurement of frequencies in the infrared spectrum in the range below 400 cm^{-1}). A molecule often has a number of identical frequencies (degeneracy with respect to symmetry or accidental degeneracy). It is impossible to detect this effect experimentally. A knowledge of the complete vibrational spectrum is absolutely necessary, for example, for calculating the thermodynamic functions of a molecule.

We can also find the amplitudes of the displacements of atoms from their equilibrium positions during vibrations or the amplitudes of the changes in the equilibrium geometric parameters of the molecule, that is, the mode of the vibration. The fundamental importance of calculations of this type is obvious, since they provide a basis for the interpretation of spectra. Calculation methods make it possible to determine sufficiently accurately which groups are producing the vibrations responsible for the appearance of various frequencies in the spectra. It must be stated directly that all present-day interpretation of spectroscopic data is based to a certain extent on the appropriate calculations.

There are many papers devoted to the calculation of the frequencies and modes and to determination of the force constants. Work by Soviet authors has some advantages over other work. In the first place, all the work has been carried out in a single system of coordinates by a single procedure for complete classes of compounds, and this has made it possible to obtain data which are comparable for different molecules and also to create a single set of force constants, and in the second place the authors have tried to select a potential function in general form with allowance for all possible interactions. A list of molecules for which theoretical studies have been carried out in the USSR is given in the Appendix (p. 227).

The proportion of the total number of spectroscopic studies devoted to calculation is quite insufficient. This is particularly true of the spectra of inorganic compounds, where it is difficult to make extensive use of existing

methods of calculation, for purely objective reasons (the impossibility of using for the calculations the spectra of isotopically-substituted molecules and the absence of homologous series).

Another noteworthy feature is that the methods of calculating the frequencies and modes of vibrations are as yet used only very rarely to solve various problems of molecular structure. The great majority of calculations which have been carried out, aimed at interpreting the observed spectra, are based on a molecular structure which is already known. This approach was unavoidable until a basic set of force constants for polyatomic molecules had been developed. It is now desirable, however, that these methods should be widely introduced into spectroscopic laboratory practice, particularly since the use of fast computers makes it possible to test many models without great effort.

In particular, computer methods are indispensible in spectroscopic studies aimed at investigating the influence of various types of substitution, breakdown in the geometric structure, etc. As shown above, here the observed changes in the frequencies in the spectra may be related to a change in the force field of the molecule or to a change in the masses or geometric parameters.

A characteristic example in this connection is that of the stretching vibrations of the C≡N bond in the HCN, CH_3CN, CCl_3CN, and $(CN)_2$ molecules. The frequencies and intensities of the absorption bands due to the C≡N vibrations in these molecules differ appreciably (for example, the frequencies have the values 2089, 2267, 2256, and 2329 and 2149 cm^{-1} respectively). At first sight the experimental data indicate a significant difference in the properties of the C≡N bonds in these compounds. This explanation has in fact been put forward [54], but theoretical analysis [39,44,45] has shown that the force and electro-optical parameters of the C≡N bond remain almost unchanged in the above series of molecules and that the appreciable changes in the corresponding frequencies and intensities of the absorption bands are due chiefly to the influence of kinematic factors. Another example is provided by the molecules of *gem*-dinitroethane and trinitromethane, whose spectra show a marked displacement of the frequencies of the so-called symmetrical stretching vibrations of NO_2[1402 cm^{-1} and 1343 cm^{-1} for $C_2H_4(NO_2)_2$ and 1371 cm^{-1} and 1305 cm^{-1} for $HC(NO_2)_3$]. Appropriate calculation [55] showed that this displacement can also be attributed entirely to kinematic factors. Allowance can readily be made for these effects using calculation methods. This, of course, is not the only value of calculation methods. Often it is possible to obtain extremely valuable information on molecular structure. For example, theoretical analysis of the frequencies of the normal vibrations and the intensities of the absorption bands in the IRS of the molecules of butadiene, hexatriene, and other linear polyenes with longer chains [56] has made it possible to study the important problem of double-bond conjugation. In particular, it was shown that in the ground electronic state of the molecules with alternating double and single bonds there is appreciable bond interaction due to partial displacement of the π-electron density from the double bonds to the single bonds. No tendency towards further levelling of the bond orders takes place with increase in the length of the polyene chain. It was also shown that in conjugated molecules in the stationary state the intramolecular mutual influence of substituents is rapidly extinguished with increase in the length of the conjugated chain, despite the π-electron delocalisation.

In the study of characteristic vibrations, calculation methods help to establish the maximal group of atoms whose vibrations will exhibit the property of characteristic nature of a given type. In particular, theoretical study of the characteristic nature of the vibrations has shown that the reproducebility of various frequencies in a spectrum does not always indicate that the vibration is localised. This must be taken into account in experimental practice. A rigorous solution to the problem of the characteristic nature of vibrations of given functional groups can be obtained only on the basis of appropriate theoretical analysis. In this, in order to determine the smallest group of atoms responsible for a given characteristic frequency, it is sufficient to know merely the orders of magnitude of the force constants. By then calculating the sensitivity of this frequency to changes in various quantities characterising the molecule as a mechanical system, it is possible to investigate the influence of the quantities used in the calculation and sometimes the nature of the changes in this frequency on going to other molecules.

The calculation of the sensitivity of the characteristic frequencies to change in various quantities for three-dimensional molecular configurations can be used successfully to identify rotational isomers of certain molecules from the vibrational spectra.

Calculation methods should undoubtedly play an important part in the study of intermolecular interactions and molecular association, where the interpretation of the observed changes in the spectra often presents an extremely complex problem.

The importance of theoretical methods in vibrational spectroscopy will undoubtedly increase greatly in the near future.

4. FORCE CONSTANTS OF POLYATOMIC MOLECULES AND THEIR DETERMINATION

The most important problem in vibrational spectroscopy is to determine the coefficients K_{ij} in the expression for the potential energy. A knowledge of these quantities is necessary for carrying out numerical calculations on the vibrational spectra of polyatomic molecules. For the determination of the coefficients τ_{ij} in the expression for the kinetic energy it is sufficient to have information on the geometric structure of the molecule and the distribution of the masses, obtained independtly using other methods for studying molecules, but in the present state of the theory the force constants can in practice be determined only on the basis of experimentally measured frequencies of vibrations. This type of problem is described as the inverse spectroscopic problem and is specific for the theory of molecular vibrations.

In the study of polyatomic molecules a characteristic closed logical circle has developed: numerical calculations on molecular spectra require the introduction of quantities which are themselves found from these spectra. A way out of this situation is possible only because it has been found that some force constants can be put equal to zero and, moreover, that the force constants corresponding to individual additive groups remain unchanged within certain limits in a series of molecules containing these groups. This makes it possible to use the numerical values of the force constants, found from some molecules, for calculations on the spectra of related compounds. A consequence of this is the restriction of the possible

application of the theory chiefly to calculations on organic compounds.

When force constants are used for numerical calculations of spectra and for reaching conclusions regarding the structure of a molecule and the nature of chemical bonds it is necessary to understand clearly the physical significance of the quantities and their complex nature. Force constants depend not only on the properties of interatomic forced but also on the method adopted for describing the vibrations (the system of coordinates).[52] The same model of interatomic forces will be expressed in different ways in different systems of coordinates. In the general case when interactions take place between all the atoms, the force constants will not be characterised merely by the individual structural elements but will depend on the properties of the whole molecule.

It may be said that the force constants are representations of the elastic properties of the interatomic forces in the system of coordinates selected. Thus the choice of a working system of coordinates should correspond to the model of interatomic forces adopted. A criterion of the correspondence between the model and the system of coordinates is the smallness of the elements K_{ij} $(i \neq j)$ compared with K_{ii} $(K_{ii} \gg K_{ij})$. This requirement in turn arises because here the vibrations of the molecules can be described by the minimum number of empirical parameters (force constants); this is fundamental, since, as already noted, they are determined on the basis of experimental data on the frequencies of vibrations.

Let us examine briefly various models of interatomic forces.

Central-forces model. The central-forces model involves the assumption that the forces of interaction between all pairs of atoms depend only on the distance between the atoms and act along the straight line joining them. This model has not justified itself and is now almost never used. The inadequate nature of the model is particularly clearly seen for the bending vibrations of linear molecules. The frequencies of these vibrations should then be equal to zero, but this contradicts experimental results.

Valency-forces model. The valency-forces model is free from the above difficulties associated with the central-forces approximation for linear molecules and is closer to chemical ideas regarding interatomic forces. It is thus not accidental that the valency-forces model gives much better results in the great majority of cases. This model has formed the basis for all fundamental calculations on the spectra of polyatomic molecules in the Soviet Union and for the creation of a set of force constants suitable for the theoretical analysis of a very large number of compounds. In this model we consider the forces related to the change in the bond lengths, valency angles, and other elements forming the natural vibrational coordinates. In the expression for the potential energy it is usual to introduce, in addition to the elements K_{ii}, a series of small elements K_{ij}, that is, to use the valency-forces model not in the pure form but with slight corrections. The chief advantage of this approximation is the possibility of examining the individual structural elements of the molecule, which may be expected to be sufficiently closed units, and thus to reduce the problem of the force field of the molecule to the problem of studying the properties of its individual elements. The following rules have been empirically established for selecting the force constants in this model in the system of coordinates formed by the changes in the bond lengths, valency angles, etc.

1. The largest force constants are encountered for the bond stretching coordinates; the force constants for the other coordinates are smaller by approximately one order of magnitude.

2. The constants K_{ij} $(i \neq j)$ usually must be taken into account only for coordinates having common atoms (for angular coordinates, a common bond). This rule applies usually, but there may be exceptions. It is difficult to verify it accurately, since the attempt to find the values of force constants from experimental data is usually made (see below) on the assumption that this rule applies.

Unfortunately, these rules do not eliminate the arbitrariness in the choice of force constants, although they limit it to some extent. This intermediate character is still appreciable, and this is the weakest aspect of the present-day theory of the vibrational spectra of polyatomic molecules. Thus the actual calculations on the spectra in many instances are model calculations and this must be taken into account when theoretical methods are used to solve a given spectrochemical problem.

Analysis of the experimentally-obtained expressions for the potential energy shows that the appearance of the elements K_{ij} $(i \neq j)$ often leads to a change in the corresponding elements K_{ii}, that is, a definite functional relationship exists between K_{ij} and K_{ii}. This relationship is not examined in the valency-forces approximation. An attempt to take account of this functional relationship is made in the approximation of Urey and Bradley, which is based on an approximation of the valency-forces type but which includes several additional terms corresponding to central forces between atoms which are not joined by valency bonds. With the inclusion of the extra coordinates thus produced in the force-constants matrix, there appear coefficients for the interaction of the bonds with one another and the angle, with a simultaneous change in their force constants. Thus the introduction of the force constant for the interaction of the pair of terminal atoms in addition to the angular elasticity in the same valency angle to some extent makes it possible to take account of the above relationship between the different force constants by means of a single parameter. In the method of Urey and Bradley, however, linear terms appear in the expression for the potential energy of the vibrations. In addition to a number of contradictions which then arise, this feature leads to complication of the mathematical formalism. The Urey–Bradley approximation has not found extensive application in the Soviet Union. In practice it has no advantages over the valency forces approximation (with the addition of certain non-diagonal elements) and for many molecules it is not satisfactory and requires refinement.

In practical calculations of the frequencies and modes of molecular vibrations, use is made of the values of the force constants of bonds and groups of atoms, on which a large volume of material has accumulated. In the USSR all calculations are carried out according to a single scheme, and this has made it possible to obtain a single set of force constants. The actual force constants are found from experimental data on frequencies of vibrations. Their number, even if we neglect many non-diagonal elements, is generally found to be greater than the number of experimentally observed frequencies for a single mole-

cule. Thus the determination of the force constants of a molecule entirely from its spectrum, that is, a rigorous solution of the inverse spectroscopic problem, its impossible. It becomes possible, however, if we impose a number of additional conditions, and also make use of the spectra of isotopically substituted molecules (for which it may be assumed with sufficient accuracy that K_{ij} do not change) and the spectra of molecules of a homologous series. Considerable work has been done in this direction and an extensive set of force constants has been developed, making it possible to carry out model calculations of the frequencies and modes of vibrations, and to solve a variety of problems associated with the estimation of the characteristic nature of vibrations, the influence of substitution, etc., for almost any class of organic compound.

The material at present available on force constants is scattered in a large number of original papers. The appendix to the present review (p. 227) gives the values of the force constants characterising the elastic properties of the bonds and valency angles in some of the most important groups of organic molecules. Table 3 gives the most reliable data obtained by sufficiently correct solution of the vibrational problem. Nevertheless it should be noted that the numerical values of some of the force constants given in Table 3 must be regarded as provisional, particularly in the study of the vibrations of other molecules§.

In view of its unique importance, let us consider the problem of the determination of the force constants on the basis of experimentally-measured frequencies. Let us make use of the property of the quasidiagonality of the force-constants matrix, that is, the property $K_{ii} \gg K_{ij}$, which can be taken as proved, since there are no exceptions in all the molecules which have been studied up to the present. We shall restrict ourselves initially to the simplest case in which the values of the squares of the frequencies are close to the values of the diagonal elements. This is often encountered in practice. We shall moreover assume that the assignment of the frequencies is already known. Let us assume that the force-constants matrix is diagonal, that is that all $K_{ij} = 0$ $(i \neq j)$. The approximate values of the diagonal force constants are then found from the formulae

$$K_{ii}^{(0)} = \frac{\lambda_{i\,\mathrm{exp}}}{\tau_{ii}},$$

where $\lambda_{i\,\mathrm{exp}}$ represents the experimental values of the squares of the frequencies of the vibrations. The set of values of $K_{ii}^{(0)}$ for all ith vibrational coordinates forms the zeroth approximation of the force-constants matrix¶. The values of $\lambda_i^{(1)}$ for variation of the force constants by the quantity ΔK_{ij} can obviously be written in the form

$$\lambda_i^{(1)} = \lambda_i^{(0)} + \sum_{i,j} \left(\frac{\partial \lambda_i}{K_{ij}}\right)_0 \Delta K_{ij}, \qquad (4)$$

where $\lambda_i^{(0)}$ represents the eigenvalues of the secular equation with the force matrix in the zeroth approximation. Here it is necessary to impose certain restrictions on the values of ΔK_{ij}; the values of $\lambda_i^{(1)}$ calculated from the approximate formulae of type (4) should agree within the limits of permissible error with the values calculated by exact solution of the secular equation. The derivatives $\left(\frac{\partial \lambda_i}{\partial K_{ij}}\right)_0$ of λ_i with respect to the force constants for a given force-constants matrix are readily calculated[52]. The summation is carried out with respect to all varying force constants, which are regarded as independent. In order to simplify the subsequent notation we shall replace the double subscript for the force constants by a single subscript, arranging all the force constants in a definite order.

By varying ΔK_j within the above range, we can obtain different values of $\lambda_i^{(1)}$. We shall write $\lambda_i^{(1)} = \lambda_{i\,\mathrm{exp}} + \alpha_i$, where α_i represents certain fractions. We then have

$$\alpha_i = \lambda_i^{(0)} - \lambda_{i\,\mathrm{exp}} + \sum_j \left(\frac{\partial \lambda_i}{\partial K_j}\right)_0 \Delta K_j.$$

The problem of constructing a force-constants matrix from the given set of squares of the normal vibration frequencies will be solved (where solution is possible with the restrictions noted above) if we can select values of ΔK_j such that all $\alpha_i = 0$. This is equivalent to finding a solution for a system, of nth order, of non-homogeneous linear equations with respect to the unknowns ΔK_j:

$$\lambda_i^{(0)} - \lambda_{i\,\mathrm{exp}} + \sum_j \left(\frac{\partial \lambda_i}{\partial K_j}\right)_0 \Delta K_j = 0. \qquad (5)$$

This system will have a single solution if the number of variable force constants is equal to the number of experimentally observed frequencies, and an infinite number of solutions if the number of variable force constants is greater than the number of observed frequencies. The maximal number of unknown force constants for a non-symmetrical molecule is equal to $\frac{(3N-6)(3N-5)}{2}$, where N is the number of atoms in the molecule, and is hence much greater than the number of normal vibrations of the molecule $(3N - 6)$, that is, the number of $\lambda_{i\,\mathrm{exp}}$ measurable in principle for a single molecule. Thus the inverse spectroscopic problem in the general case has no single solution. It becomes soluble only when some of the force constants are assumed to be equal to zero (an approximate model for the force field of the molecule is selected) or are obtained by analogy with related compounds. In order to increase the number of observable frequencies it is possible to use isotopically-substituted molecules in addition to the main molecule. The system of equations including various isotopically-substituted molecules will be consistent since it may be assumed with a reasonable degree of approximation that the coefficients K_j remain unchanged in a series of isotopically-substituted molecules. It should be noted, however, that not all the equations related to various isotopically-substituted molecules will be linearly independent. This is due to the existence of definite correlations between λ_i for different isotopically-substituted compounds.

Despite the fact that this problem has already been discussed[145], the problem of the a priori choice of independent equations for isotopically-substituted molecules in specific instances cannot be regarded as solved. It is not clear, moreover, which force constants can be determined with greatest reliability from the available system of equations. However, the use of a set of vibration frequencies for isotopic molecules is always necessary for averaging the calculated force constants. Essentially different equations are obtained with a marked change in the masses of the atoms. Thus in practice use is made chiefly of the replacement of H atoms by D atoms and of vibrations in which these atoms play the main part.

§ The data are taken only from Soviet literature.

¶ In many instances it is convenient to use as the zeroth approximation of the force-constants matrix the product of the matrix which is the reciprocal of the kinematic-coefficients matrix from the right and the diagonal matrix of the squares of the experimental vibration frequencies.

If, however, the number of observed frequencies of the main molecule plus its isotopically-substituted derivatives is still less than the number of variable elements in the force-constants matrix, it is obviously always possible to select a set of elements ΔK_j, which will completely satisfy experiment but which will not be the only set. It is, of course, possible to impose on the variation of ΔK_j the condition that they lie within a given section, but then the set of values of ΔK_j and hence the final force-constants matrix will not be single ones, and at present there is no criterion for selecting the most reliable from the various sets, unless certain assumptions are made regarding the magnitudes of some of the force constants.

Let us next assume that the number of $\lambda_{i\,\mathrm{exp}}$ with the use of isotopic molecules becomes greater than the number of unknown elements K_j. The number of equations of type (5) for $\alpha_i = 0$ will then be greater than the number of unknowns and from these it is possible to separate various groups of equations which, generally speaking, will give various sets of ΔK_j, that is, the problem again to some extent loses its definite character. In such instances use is made of the method of least squares proposed by Gauss, and the problem is formulated as follows: we have to select values of ΔK_j which will satisfy the extra system of equations (5) with the highest degree of probability. It is possible to satisfy all the equations only with a certain error $\Delta\alpha_i$, that is, for the values of ΔK_j being sought we have:

$$\Delta\alpha_i = \lambda_i^{(0)} - \lambda_{i\ \mathrm{exp}} + \sum_j \left(\frac{\partial\lambda_i}{\partial K_j}\right)_0 \Delta K_j \text{ (for all values of } i).$$

These values will be the most probable values if $\sum_i (\Delta\alpha_i)^2$ has its smallest value, which is possible for values of ΔK_j satisfying the conditions $\frac{\partial}{\partial K_j}\left[\sum_i (\Delta\alpha_i)^2\right] = 0$, which lead to a system of non-homogeneous linear equations whose order is equal to the number of unknowns ΔK_j. By solving this system of equations we find a single set of ΔK_j and hence the force-constants matrix.

The method of least squares can also be extended to where the initial approximation for the force-constants matrix is not sufficiently close to the true one for linear extrapolation to be satisfactory [146].

In the solution of the problem by the method of least squares according to the scheme described it is necessary to make allowance for the following important features. Firstly, considerable arbitrariness may be introduced in the formulation of the differences $\lambda_i^{(0)} - \lambda_{i\,\mathrm{exp}}$ (particularly if $\lambda_i^{(0)}$ differ greatly from $\lambda_{i\,\mathrm{exp}}$). As a result, different solutions of the inverse problem will be obtained for different combinations of $\lambda_i^{(0)}$ and $\lambda_{i\,\mathrm{exp}}$. It can be shown, for example, that the number of solutions of the inverse problem for a single molecule with $3N - 6$ force constants to be determined, for a given set of $3N - 6$ squares of experimental frequencies, is equal to $(3N - 6)!$ [147]. It can also be shown that not all of these solutions satisfy isotopically substituted molecules; when the frequencies of the vibrations of certain isotopically substituted derivatives are used in addition to the frequencies of the single molecule, this makes it possible to decrease the arbitrariness in the choice of the single solution. At present, however, we do not have at our disposal methods which in the solution of the problem according to the scheme described would make it possible, for all isotopically substituted molecules, to select in advance combinations of $\lambda_i^{(0)}$ and $\lambda_{i\,\mathrm{exp}}$ in the differences between the calculated and experimental squares of the frequencies such that the above arbitrariness would be decreased to the maximal extent or eliminated. This becomes possible only when the selection of the zeroth approximation of the force-constants matrix is so successful that the frequencies of the vibrations calculated on this basis are close to the experimental values for all isotopic molecules and the interpretation of the frequencies is known.

It should also be noted that when the method of least squares is used to solve the inverse spectroscopic problem it is strictly speaking necessary to take account of the statistical weights of the squares of the experimental frequencies and this introduces difficulties associated with the fact that it is not always clear which physical principles should form the basis of the selection of the values of these weights.

It is also important to understand that the use of the simple method of least squares is in general justified only when the quantities obey the Gaussian distribution and the number of equations used is much greater than the number of force constants to be determined. These two conditions are comparatively rarely satisfied in practice, however.

An undoubted advantage of the method is the simplicity of the mathematical formalism, and this is the main reason why this method has recently found extensive application.

There is another possible method for solving the inverse problem of determining the values of the force constants of a molecule from the given frequencies of its vibrations; this method is convenient chiefly in that it does not require the formulation of differences between experimental and calculated squares of the frequencies, where, as already noted, a certain arbitrariness may be introduced. Here it is most natural to use as experimental points not the numbers $\lambda_{i\,\mathrm{exp}}$, but their combinations. In particular, we can obtain a non-linear system of equations for the values of K_j being sought; these are used since the equation for determining λ_i, with the usual form:

$$\mathrm{Det}\begin{pmatrix} (d_{11} - \lambda); d_{12}; \ldots; d_{1n} \\ \ldots\ldots\ldots\ldots \\ d_{n1}; d_{n2}; \ldots; (d_{nn} - \lambda) \end{pmatrix} = 0,$$

is equivalent to the equation

$$\lambda^n + p_1\lambda^{n-1} + p_2\lambda^{n-2} + \ldots + p_n = 0,$$

where p_1 is a function of the first powers of K_{ij}, p_2 a function of the squares and paired products of K_{ij}, etc. The coefficients p_i are in turn related to λ_i by the relationships:

$$p_i = (-1)^i \sum_{1 \leqslant n_1 < n_2 \ldots < n_i < n} \lambda_{n1}\lambda_{n2}\lambda_{n3} \ldots \lambda_{ni}.$$

Thus the problem of determining K_{ij} can be reduced to the solution of the non-linear system of equations:

$$p_i = (-1)^i \Sigma\lambda_{n_1} \ldots \lambda_{ni}.$$

In practice it is more convenient to use not this system of equations but the system converted into the form $p_i' = \sum_n \frac{1}{i}\lambda_n^i$. This can be done by taking account of the fact that the quantities $\sum_n \lambda_n^i$ and p_i are related to one another by simple relationships. This last system of equations can be solved if even only the orders of magnitude of the force constants are known and it is possible to construct

in approximate force-constants matrix; it is significant that it may differ from the true one to a much greater extent than is possible when the method of least squares is used. Approximate matrices of this type can almost always be constructed if account is taken of the fact that usually the interpretation of the spectra of polyatomic molecules begins with the simplest molecules of the selected homologous series, which generally exhibit fairly high symmetry, so that when symmetry coordinates are used and the stretching and bending vibrations are separated approximately, we obtain secular equations and equations of extremely low degrees for determining force constants. As a result of work by a number of authors there has now been created such an extensive set of force constants for individual atomic groups and molecules that a rough approximation of the force-constants matrix can be constructed for almost any organic molecule. We can thus start from a certain approximation for the force-constants matrix. It is then possible, for the solution of the system of equations

$$p_i' = \sum_n \frac{1}{l} \lambda_n^i \text{ exp (for all values of } i), \qquad (6)$$

to use the so-called method of steepest descents[148]. The method of solution can be demonstrated by the following illustrative geometric method. Let us assume that we have a certain surface Φ (1), inside which we have a point corresponding to the solution of the system. The initial approximation is given by a certain point on the surface. We draw a perpendicular to the surface and move along it. The function Φ, which has the significance of the "distance" of the moving point from the solution of the system (the point *O*), will then decrease until it reaches point 2, the closest point on the perpendicular to point *O*, after which it will begin to increase. We then take point 2 for the start of a new process and construct a new perpendicular to the surface, passing through this new point [Φ (2)]. By moving along this perpendicular, we find a point 3 which will now lie much closer to the solution being sought, etc.

A disadvantage of the method described is that the system of equations being considered, in the range of force constants in which we are interested, may have more than one solution. In order then to find all the solutions or to satisfy ourselves that the solution obtained is the single solution, we must select different initial points on the surface $\Phi(k)$, separated as far as possible from one another. A choice of solution corresponding to the true set of force constants (the set having physical significance) can then be made only be studying isotopically substituted molecules and homologous series.

The methods described are extremely tedious and their use requires the extensive application of electronic computers. In practice, in the great majority of investigations, the force constants are found by selecting (varying) them within a definite range until satisfactory agreement is obtained between λ_i and the experimental values $\lambda_{i\,\text{exp}}$ (method of trial and error). To facilitate the variations, a set of partial derivatives of λ_i with respect to the force constants is usually also calculated. Unfortunately, this type of approach involves a considerable contribution from factors which are difficult to take into account, such as the experience and intuition of the author.

Thus the solution of the inverse spectroscopic problem involves appreciable difficulties. In the great majority of instances it is, in general, impossible to determine the force-constants matrix without making assumptions regarding the magnitude of some of its elements. Such approximations, as already noted, include the assumptions that the non-diagonal elements are small compared with the diagonal elements, that the force constants of the interaction of coordinates at a distance from one another are equal to zero, and that the force constants of the individual atomic groups in a series of similar compounds remain unchanged. These assumptions are based on a definite view of the nature of chemical forces in a molecule and the existence of characteristic vibrations.

With certain assumptions, these methods can also be extended to the study of homologous series. In doing so, some of the force constants are always put equal to zero, and some are assumed to be unchanged at least within a range of two to three adjacent molecules in a series. It is on this basis that an appreciable set of force constants has been created for molecules and functional groups, shown to be completely satisfactory for many calculations on specific compounds. It should be remembered, however, that because of the limitations noted above, the force constants are obtained with a certain error, which may be particularly large in the non-diagonal elements. A major shortcoming is the impossibility at present of making an objective estimate of this error. At the present stage, however, this feature presents almost no restriction to the study of the frequencies and modes of vibrations of polyatomic molecules, but it must be taken into account in all attempts to compare the values of force constants and other molecular parameters. It is for this reason that in a number of instances little trust can be put in the comparison of force constants and interatomic distances, bond energies, etc., frequently encountered in the literature.

The most reliable set of force constants is that which describes sufficiently accurately the frequencies of vibrations of a given molecule and its available isotopically substituted derivatives, and is preserved in the closest members of a homologous series.

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The development of studies of polyatomic molecules by the methods of vibrational spectroscopy are characterised primarily by the ever-increasing use of theoretical analysis to solve applied problems. The reason for this is to be found in the constant increase in the complexity of the materials and problems being studied and also in the gradual recognition by experimental workers of the fact that in principle it is only on the basis of theoretical analysis that it is possible to distinguish more or less confidently the various factors leading to the phenomena observed in spectra and to reach sufficiently well-founded conclusions regarding intramolecular interactions. The choice of appropriate spectroscopic characteristics for the solution of applied problems should also be based on theoretical analysis. Thus modern spectrochemical study must consist of a close combination of experiment and calculation of the spectrum for a model of the molecule being studied.

The need arises, however, for extensive calculations, so that theoretical methods cannot be introduced into practical spectrochemical studies until the entire calculation side has passed completely to electronic computers and is in fact reduced to the form of the input to be supplied

to the computer. Considerable progress has been made in this direction in recent years. Programmes have appeared which not only solve the equations for the vibrations but also formulate them[20] and also carry out a number of other operations. The situation is much less satisfactory in the development of programmes for solving the inverse spectroscopic problem and for the automatic interpretation of the spectra for homologous series. The existing programmes are far from perfect and their possibilities are extremely limited.

The extensive use of electronic computers in spectrochemical practice makes it possible, with very little expenditure of effort (for example, the preparation of material for the calculation for a molecule containing 9–10 atoms according to a programme developed by one of the present authors[20] occupies a total of 2–2½ h) and in a short time to carry out a large number of calculations for the selected molecules in order to establish the characteristic nature of the vibrations, the reasons for the displacements of the frequencies as a result of given substitutions, etc. It has also become possible to use theoretical methods for the analysis of a variety of regular features and to assign frequencies in those compounds for which the system of force constants is as yet insufficiently developed.

At the same time another extremely important problem is being solved; it is becoming possible for proper numerical calculations for the spectra of molecules to be carried out by persons who are not completely equipped with the mathematical apparatus of the theory. The latter is not necessary using the system of programmes developed, paradoxical as it may seem at first glance. Thus it is possible to confound the great principle: "No one can comprehend the infinite!" and to bring modern theoretical methods to a wide range of spectroscopists without imposing upon them the great additional task of studying a number of new disciplines.

The calculation methods of the theory, based on electronic computers, give to research workers a powerful tool for the study of spectra, but it is necessary to understand the use of this tool. The chief difficulty in the practical application of modern theoretical methods, after the transfer of all the calculation side to electronic computers, lies in the choice of problem in which these methods can be applied with the greatest efficiency.

The study of vibrational spectra has become one of the fundamental means of investigating the structure and properties of polyatomic molecules. It is difficult even to list approximately the vast range of problems which are solved by the methods of vibrational spectroscopy. These methods are far from having exhausted their possibilities. There is no doubt that in the near future we shall witness considerable progress in this branch of science. This requires primarily the extensive introduction of theoretical methods which have already been developed and which until recently were the acquisition of a narrow group of specialists, into everyday practice in spectroscopic laboratories. This will undoubtedly result in a sharp raising of the level of spectrochemical studies. This process is already taking place, as indicated, in particular, by the continuously increasing proportion of papers dealing with calculations.

At the same time the next urgent problem concerns the further improvement of the theory itself and the development of new aspects of the theory. Unfortunately, it must be stated that this work is not proceeding rapidly enough at present.

5. APPENDIX

Table 2 lists the compounds whose vibrational spectra have been calculated as a result of work published in Soviet literature up to the middle of 1964. The formulae for isotopically substituted molecules whose spectra have been used to determine the set of force constants are given in parentheses after the name of the compound.

TABLE 2.

Methane (CH_4, CH_3D, CH_2D_2, CHD_3, CD_4)[14]; ethane (C_2H_6, C_2D_6)[14]; propane[14,57,58]; butane[57-59]; isobutane ($HC(CH_3)_3$, $DC(CH_3)_3$)[14,61]; 2,3-dimethylbutane[62]; pentane[60]; isopentane[14]; neopentane[14]; cyclopropane (C_3H_6, C_3D_6)[63]; methylcyclopropane[64]; 1,1-dimethylcyclopropane[64]; cyclobutane[65]; cyclopentane (C_5H_{10}, C_5D_{10})[66-69]; cyclohexane (C_6H_{12}, $C_6H_{11}D$, C_6D_{12})[70,71]; methylcyclohexane[72]; ethylcyclohexane[73]; *trans*-1,4-dimethylcyclohexane[71]; *cis*-1,3,5-trimethylcyclohexane[71]; halogeno-derivatives of methane[14,41]; chloro-derivatives of ethane[14]; methanol (CH_3OH, CH_3OD, CD_3OH, CD_3OD)[14]; methanethiol[14]; ethylene (C_2H_4, C_2H_3D, C_2HD_3, *asym*-$C_2H_2D_2$, *trans*-$C_2H_2D_2$, *cis*-$C_2H_2D_2$)[14,73,74]; propene (C_3H_6, C_3D_6)[75]; but-1-ene[75]; *cis*-but-2-ene[76]; *trans*-but-2-ene[76]; isobutene[77]; *cis*- and *trans*-isomers of ethylene[79,80]; 2,3-dimethylbut-2-ene[76]; penta-1,4-diene[78]; halogeno-derivatives of ethylene[81,82]; allene (C_3H_4, HDC_3H_2, $D_2C_3H_2$, C_3D_4)[83,85]; methylallene[85]; 3-methylbuta-1,2-diene[78]; cyclobutene (C_4H_6, C_4D_6)[84]; butadiene (C_4H_6, C_4D_6)[86,86]; acetylene (H_2C_2, HDC_2, D_2C_2)[39]; methyl vinyl ether[87]; methyl vinyl sulphide[88]; hydrogen cyanide (HCN, DCN)[89]; acetonitrile (CH_3CN, CD_3CN)[44]; mono-, di-, and tri-chloroacetonitriles[48]; cyanamide (H_2NCN, D_2NCN)[89]; nitromethane (CH_3NO_2, CD_3NO_2, $CH_3N^{18}O_2$)[90]; nitroethane[90]; *gem*-dinitroethane[88]; trinitromethane ($HC(NO_2)_3$, $DC(NO_2)_3$)[88]; silane (SiH_4, SiH_2D_2, $SiHD_3$, SiD_4)[91]; methylsilane (CH_3SiH_3, CH_3SiD_3)[92,93]; dimethylsilane[93]; trimethylsilane[92]; tetramethylsilane ($Si(CH_3)_4$, $Si(CD_3)_4$)[94]; halogenomethylsilanes[96-99]; disilane (Si_2H_6, Si_2D_6)[100]; chloromethylgermanes[101]; germanium tetraiodide[102]; benzene (C_6H_6, C_6H_5D, $C_6H_4D_2$, $C_6H_3D_3$, $C_6H_2D_4$, C_6D_6)[103-108]; toluene ($C_6H_5CH_3$, $C_6H_5CD_3$)[106-108]; ethylbenzene[109]; isopropylbenzene[110]; *o*-xylene[111,112]; *m*-xylene[113]; *p*-xylene[114]; 1,3-diethylbenzene[115]; mesitylene[116,117]; durene[116,117]; 1,2,3-trimethylbenzene[118]; biphenyl ($C_{12}H_{10}$, $C_{12}H_9D_4$, $C_{12}H_4D_6$, $C_{12}D_{10}$)[119-121]; naphthalene ($C_{10}H_8$, α-$C_{10}H_4D_4$, β-$C_{10}H_4D_4$, $C_{10}D_8$)[122-124]; pyridine (C_5H_5N, 4-C_5H_4DN, 2-C_5H_4DN, 3-C_5H_4DN, 2,6-$C_5H_3D_2N$, 3,5-$C_5H_3D_2N$, C_5D_5N)[125,126]; pyrazine[127]; *sym*-triazine ($C_3H_3N_3$, $C_3D_3N_3$)[127]; *sym*-tetrazine ($C_2H_2N_4$, C_2HDN_4, $C_2D_2N_4$)[127]; the cyclopentadienyl ring of ferrocene (C_5H_5, C_5D_5)[128]; the hydroperoxide group (C—O—OH)[129]; trimethyl phosphate[130]; trimethyl thiophosphate[130]; phosphorus oxide trichloride[131]; phosphorus ovide tribromide[131]; phosphorus sulphide trichloride[131]; phosphorus sulphide tribromide[131]; ammonia (NH_3, ND_3)[14]; methylamine (CH_3NH_2, CD_3NH_2, CH_3ND_2, CD_3ND_2)[132]; boron trifluoride–ammonia ($F_3B.NH_3$, $F_3B.NH_2D$, $F_3B.NHD_2$, $F_3B.ND_3$)[133]; the tetrahalides of C, Si, Ge, Ti, Sn, and Pb[134]; boric oxide ($^{10}B_2O_3$, $^{11}B_2O_3$, $^{10}B^{11}BO_3$)[135]; boron sulphide ($^{10}B_2S_3$, $^{11}B_2S_3$)[135]; SF_4[136]; SF_3Cl[137]; titanium tetrachloride[138]; silicates[139-141]; the UO_2^{2+} ion[142]; water (H_2O, D_2O, HTO, DTO, T_2O)[143]; hydrogen sulphide (H_2S, D_2S, HDS, DTS, HTS, T_2S)[143,144]; hydrogen selenide (H_2Se, HDSe, D_2Se, HTSe, DTSe, T_2Se)[143].

TABLE 3. Force constants $\times 10^6$ (cm^{-2}).

Compound	Coordinates *i* and *j*	K_i	K_j	K_{ij}	References
Ethane H_3C-CH_3		8.34	8.34	0.05	14
		8.34	7.02	0.05	
		7.02	0.92	0.43	
		8.34	0.71	0.35	
		0.92	0.71	−0.035	
Propane $H_3C-CH_2-CH_3$		7.02	7.02	0	14, 57, 58
		7.02	0.80	0.43	
Fluoromethane H_3CF		8.53	9.80	0.30	14
		9.80	1.56	1.25	
		0.76	1.56	0.12	

TABLE 3 (contd.)

Compound	Coordinates i and j	K_i	K_j	K_{ij}	References
Chloromethane H_3CCl		8.53	5.80	0.15	14, 41
		5.80	1.10	0.80	
		0.75	1.10	0.12	
Bromomethane H_3CBr		8.53	4.60	0.10	14, 41
		4.60	0.95	0.65	
		0.73	0.95	0.11	
Iodomethane H_3CI		8.53	3.90	0.08	14, 41
		3.90	0.85	0.55	
		0.72	0.85	0.10	
Methanol H_3C-OH		8.0	12.65	0	14
		12.65	1.15	0.40	
Methanethiol H_3C-SH		5.0	6.5	0	14
		6.5	1.05	0.50	
Methylamine H_3C-NH_2		10.77	10.77	0.05	132
		10.77	8.60	0.05	
		10.77	0.80	0.40	
Ethylene $H_2C=CH_2$		14.2	8.63	0.10	14, 73, 74
		8.63	8.63	0.03	
		14.2	0.80	0.45	
		8.63	0.58	0.37	
		0.80	0.58	−0.035	
Propene $H_2C=CH-CH_3$		14.2	7.02	0.10	75
2-Methylpropene $H_2C=C(CH_3)_2$		7.02	7.02	0	78
Fluoroethylene $H_2C=CFH$		15.00	10.20	0.50	81
		15.00	1.07	1.00	
		10.20	8.82	0.30	
		10.20	0.73	1.00	
Chloroethylene $H_2C=CClH$		14.20	6.00	0.28	81
		14.20	1.11	0.80	
		6.00	8.80	0.15	
		6.00	0.69	0.66	
Allene $H_2C=C=CH_2$		15.05	15.05	0.15	83, 85
		15.05	8.55	0.25	
1,2-Butadiene $H_3CHC=C=CH$		15.05	15.05	0.15	85
		15.05	7.02	0.10	
1,3-Butadiene $H_2C=CH-CH=CH_2$		12.00	10.40	0.40	58
		12.00	12.00	−1.50	
		12.00	8.63	0.10	
Acetylene $HC\equiv CH$		24.48	9.85	0.20	39
Hydrogen cyanide HCN		27.70	9.70	0.20	39
Acetonitrile H_3C-CN		27.70	8.10	0.20	44

TABLE 3 (contd.)

Compound	Coordinates i and j	K_i	K_j	K_{ij}	References
Trichloroacetonitrile Cl_3C-CN		27.70	7.80	0.20	45
		7.80	5.40	0.10	
		7.80	1.55	0.85	
		5.40	1.50	0.60	
Nitromethane H_3C-NO_2		14.00	14.00	1.60	90
		7.67	14.00	0.35	
		14.00	1.95	0.55	
		7.67	1.26	0.60	
		1.95	1.26	−0.06	
Disilane $H_3Si-SiH_3$		4.51	4.51	0.03	100
		4.51	2.75	−0.008	
		2.75	0.602	0.30	
		4.51	0.72	0.23	
		0.602	0.72	0.084	
Methylsilane H_3C-SiH_3		5.11	4.31	−0.008	92, 93
		5.11	0.932	0.346	
Chlorotrimethylsilane $Cl-Si(CH_3)_3$		5.077	4.00	0.080	96
		5.077	1.247	0.35	
		5.077	0.845	0.35	
Chlorotrimethylgermane $Cl-Ge(CH_3)_3$		4.48	2.75	0.08	101
		4.48	1.245	0.35	
		4.48	0.68	0.40	
		1.245	1.245	0.315	
Benzene C_6H_6		11.36	11.36	1.04	103–105
		11.36	11.36	−0.87	
Ammonia H_3N		10.72	10.72	0.05	14
		10.72	0.79	0.40	
		0.79	0.79	−0.07	

Table 3 summarises the force constants of bonds and valency angles and also the constants for their interaction for some of the most important atomic groups in organic molecules.

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NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME ELECTRON-DEFICIENT COMPOUNDS: BORON HYDRIDES, DIMERS OF ALKYLALUMINIUMS, AND ORGANOLITHIUM COMPLEXES

I. B. Golovanov and A. K. Piskunov

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INTRODUCTION

Many compounds are known in which the number of chemical bonds exceeds the number of electron pairs: boron hydrides [1]; the dimers of the alkyl compounds of aluminium [2], beryllium [3], organolithium complexes [4], etc.[5,6]. Compounds of this type have become known as electron-deficient.

By use of the nuclear magnetic resonance (NMR) method information has been obtained about the structure of these compounds and also about the electron distribution and about its symmetry for certain nuclei. The most important results of the study of electron-deficient compounds by the NMR method are considered below.

Before discussing the NMR results some questions of the qualitative theory of electron-deficient bonds [1,5-7] are considered.

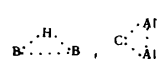
I. QUALITATIVE QUANTUM-MECHANICAL IDEAS ABOUT THE FORMATION OF ELECTRON-DEFICIENT BONDS

The presence of a metal atom with vacant orbitals on which the bond-establishing electrons can be promoted without a large expenditure of energy, and of an atom or group of atoms which do not possess unshared electron pairs are general for most electron-deficient compounds. The conditions for the formation of donor–acceptor bonds do not exist.

Compounds with electron-deficient bonds have been insufficiently studied, but it can be maintained that the principal features of the structures of these compounds are clear. Thus, the data on diamagnetic susceptibilities [2] suggest that the bonds cannot be "one-electron". Each of the bridge bonds has less energy than if it were "normal" and its length also differs from the "normal". Some examples from the compounds that have been most studied are given in Table 1.

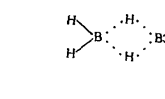
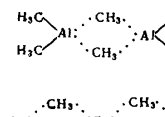
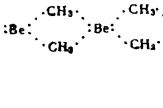
The bridge bonds B...H, Be...C, and Al...C are longer than the corresponding terminal bonds. The latter have the same length as the "usual" bonds.

The experimental values for the metal–metal distances in these compounds are close to those for the M_2 molecules. Attempts were therefore made to explain the bonding in such complexes by the formation of "protonated double bonds" [2]. Next considerations were advanced in support of the formation of polycentric orbitals [13] of the type:



Apparently a short M–M distance is necessary for the formation of localised three-centre orbitals.

TABLE 1.

Structure of the compounds		Heats of formation of the complexes (Ref. 5), kcal	r_{M-M}, sum of covalent radii (Refs. 11 and 12), Å	r_{C-C}, sum of intermolecular radii, Å
	$r_{BB}=1.78$ Å[a] $r_{BH_K}=1.19$ Å $r_{BH_M}=1.34$ Å $\angle H_K BH_K=121.5°$ $\angle H_M BH_M=100°$	32	1.82	3.8
	$r_{Al-Al}=2.55$ Å[a] $r_{Al-C_K}=1.99$ Å $r_{Al-C_M}=2.24$ Å $\angle C_M AlC_M=70°$	20	2.86	3.8
	$r_{Be-C}=1.93$ Å $\angle Be-C-Be=66°$ $r_{Be-Be}=2.10$ Å	—	2.26	3.8

The C–C distance in complexes is usually close to the van der Waals distance and the C atoms can be considered as non-bonded from the point of view of valency.

A characteristic feature is that the M–C–M angle is less than 90°, which suggests that the orbitals of the metal atoms form a bond with one orbital of the carbon atom and also that the metal atoms interact with one another. Apparently the formation of such bonds becomes hindered as the size of the metal atom is increased.

Electron-deficient bonds can differ in degree of polarity. In diborane, for example, the B...H bonds are close to covalent and in the dimer of phenyllithium they are apparently strongly polar. This can suggest starting from the characteristics of the atoms which form the bond. Table 2 gives some facts about the atoms, the bonds between which are discussed below.

Although electronegativity is a very crude characteristic of ionic character of the bonds, nevertheless it allows us to state, for example, that the C–Li bond should be more polar than B–H, etc.; therefore for organolithium complexes the contribution of the ionic state must also be considered.

Spectrographic data about the atomic levels also somewhat elucidate the problem of the use of free orbitals. Actually it is most favourable to use those orbitals for which the energy of promotion is less, and also the energy of the orbital itself is less. When the atoms are of similar size, the strength of the bond in the complex will be greater for that atom whose vacant levels are close to the occupied level with lower energy. For example, the aluminium and lithium atoms are similar in size and therefore it could be expected that the C–Li bond would be stronger than the C–Al bond. The available information about the energy of the C...Li bond confirms this hypothesis [16,17].

TABLE 2.

Property	Atoms				
	Li	Be	B	Al	C
Position of the atomic levels (occupied and lower free)[14]	—3.6...— —5.4...— E, eV				
Electronegativity[15]	0.95	1.5	2.0	1.5	2.5
Covalent radii [11,12]	1.34	0.96	0.84	1.26	0.77

Theoretically the formation of electron-deficient compounds with predominantly covalent bonds can be considered as the usual problem for quantum chemistry involving a few electrons in the field of a few centres, in which the number of atomic orbitals from which the molecular orbitals are constructed is greater than the number of electrons which participate in the bonds [1,5-7].

As the simplest example, let us consider the molecular ion $[A-B-C]^+$, the bonding in which is provided by a pair of electrons. We will consider that the atoms A, B, and C are disposed along a straight line, there is no exchange between A and C, and the overlap can always be neglected.

Then within the framework of the simplest method of LCAO MO, [18] by expressing the molecular orbital in the form

$$\psi = a_1\psi_A + a_2\psi_B + a_3\psi_C,$$

we obtain the secular equation for determining the energy:

$$\begin{vmatrix} \alpha_A - E & \beta_1 & 0 \\ \beta_1 & \alpha_B - E & \beta_2 \\ 0 & \beta_2 & \alpha_C - E \end{vmatrix} = 0.$$

When the atoms A and C are greatly different and the interaction of atom B with one of them (for example, with A) is considerably greater than that with the other, that is, $\beta_1 \gg \beta_2$, then this is equivalent to dealing with the system $[A-B]^-$ ion C^+.

The energy of an electron in the molecular orbital (we assume that $\alpha_A - \alpha_B \ll \beta$) will then be:

$$E = \frac{\alpha_A + \alpha_B}{2} + \beta.$$

When atoms A and C are the same and the ion C^+ has approached to the closest distance, then since A–B is equal in length to A–C, the secular equations will have the form:

$$\begin{vmatrix} \alpha_A - E & \beta & 0 \\ \beta & \alpha_B - E & \beta \\ 0 & \beta & \alpha_A - E \end{vmatrix} = 0$$

and the energies of the molecular orbitals will be:

$$E_1 = \frac{\alpha_A + \alpha_B}{2} + \sqrt{2}\beta,$$

$$E_2 = \alpha_A,$$

$$E_3 = \frac{\alpha_A + \alpha_B}{2} - \sqrt{2}\beta.$$

The gain in energy which is obtained in the formation of the electron-deficient compound $(A-B-A')^+$, is calculated as the difference in energy of the ion $(A-B-A')^+$ when a free orbital is used and the energy of the system consisting of the isolated molecule AB and the ion A^+ when the A orbital is not used:

$$\Delta E = 2\left(\frac{\alpha_A + \alpha_B}{2} + \sqrt{2}\beta\right) - 2\left(\frac{\alpha_A + \alpha_B}{2} + \beta\right) = 0.82\beta,$$

where ΔE is the delocalisation energy of the electron.

We note that this result is obtained with the following assumptions: (1) the atoms A and A′ are similar in properties or the same, (2) the overlaps A–B and B–A′ are the same (that is, the A–B and B–A′ bond lengths are the same), (3) the energy of promotion of the electrons in the valence state equals zero. As noted, this requirement is satisfied by some of the compounds considered above.

It can be assumed that the orbitals used by atom B should be the same in the A and A′ directions, that is, there should be known local symmetry in the structure of the complex. When atom B gives one orbital then its overlap with the atoms A and A′ should be the same.

Polycentric orbitals should be formed when there is conjugation and in electron-deficient molecules. In reality, when n orbitals are used for the formation of the "usual" two-centre bonds then $n/2$ bonding and $n/2$ anti-bonding orbitals are obtained from them. n electrons are distributed in the bonding orbitals, but the anti-bonding orbitals remain vacant. If there were more than n electrons then they would occupy some of the anti-bonding orbitals. When n orbitals are used for the formation of three-centre bonds they give $n/3$ bonding orbitals. The others will be non-bonding or anti-bonding. $2n/3$ of the electrons will be distributed in the bonding orbitals, and the remaining electrons would occupy the anti-bonding orbitals. Evidently electron-deficient compounds will be short of just those electrons which should have occupied the anti-bonding orbitals.

Besides the bonding in the complex where there is formation of polycentric orbitals with bonds close to covalent, as considered above there is a possibility of the formation of complexes due to polar bonds.

For any two-atom molecule A–B the molecular orbital can be presented in the form $\psi = a_1\psi_a + a_2\psi_b$ and the energy of the occupied orbital is

$$E = \frac{\alpha_1 + \alpha_2}{2} + \beta,$$

where

$$\alpha_i = \int \psi_i^* \mathbf{H} \psi_i \, d\tau; \quad \beta = \int \psi_1^* \mathbf{H} \psi_2 \, d\tau.$$

When the A–B bond is strongly polar, then the complex $(A-B)_2$ is formed. For simplicity we will consider it to be symmetrical, with the lengths of the bonds close to those for the monomeric molecule AB.

To describe the complex $(A-B)_2$ for the initial atomic orbitals we can select symmetrical orbitals, the form and symbolic representation of which are shown in Table 3.

The molecular orbitals are selected in the form: $\psi = \sum_i c_i\sigma_i$, in which the lowest energy is determined from the equation:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0,$$

where

$$H_{11} = \int \sigma_1 \mathbf{H} \sigma_1 d\tau = \int \frac{1}{\sqrt{2}}(\psi_{A_1} + \psi_{A_2}) \mathbf{H} \frac{1}{\sqrt{2}}(\psi_{A_1} + \psi_{A_2}) d\tau =$$

$$= \frac{1}{2}\left[\int \psi_{A_1} \mathbf{H} \psi_{A_1} d\tau + 2\int \psi_{A_1} \mathbf{H} \psi_{A_2} d\tau + \int \psi_{A_2} \mathbf{H} \psi_{A_2} d\tau\right] =$$

$$= \int \psi_{A_1} \mathbf{H} \psi_{A_1} d\tau + \int \psi_{A_1} \mathbf{H} \psi_{A_2} d\tau = \alpha_1 + \beta' = (1 + k_1)\alpha_1, \qquad k_1 > 0$$

$$H_{22} = \int \sigma_2 \mathbf{H} \sigma_2 d\tau = (1 + k_2)\alpha_2, \quad k > 0$$

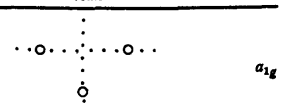
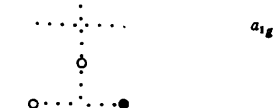
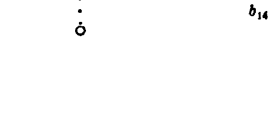
$$H_{12} = \int \sigma_1 \mathbf{H} \sigma_2 d\tau = 2\beta$$

Since all the bond lengths in the diameter are the same, the solution will be:

$$E_1 = \frac{(1 + k_1)\alpha_1 + (1 + k_2)\alpha_2}{2} + 2\beta,$$

$$E_2 = \frac{(1 + k_1)\alpha_1 + (1 + k_2)\alpha_2}{2} - 2\beta.$$

TABLE 3.

Orbital	Atoms	
$\frac{1}{\sqrt{2}}(\psi_{A_1}+\psi_{A_2})=\sigma_1$		a_{1g}
$\frac{1}{\sqrt{2}}(\psi_{B_1}+\psi_{B_2})=\sigma_2$		a_{1g}
$\frac{1}{\sqrt{2}}(\psi_{A_1}-\psi_{A_2})=\sigma_3$		b_{1u}
$\frac{1}{\sqrt{2}}(\psi_{B_1}-\psi_{B_2})=\sigma_4$		b_{1u}

We find other solutions from the equations:

$$\mathbf{H}\psi_3 = E_3\psi_3 \quad \psi_3 = \sigma_3$$
$$\mathbf{H}\psi_4 = E_4\psi_4 \quad \psi_4 = \sigma_4$$
$$E_3 = \int \sigma_3 \mathbf{H} \sigma_3 d\tau = (1-k_1)\alpha_1, \quad k_1 > 0,$$
$$E_4 = \int \sigma_4 \mathbf{H} \sigma_4 d\tau = (1-k_2)\alpha_2, \quad k_2 > 0.$$

We assume that

$$|(1-k_1)\alpha_1| > |(1-k_2)\alpha_2|.$$

The occupied orbitals have the energies:

$$E_1 = \frac{(1+k_1)\alpha_1 + (1+k_2)\alpha_2}{2} + 2\beta,$$
$$E_3 = (1-k_1)\alpha_1.$$

The difference in energy between the dimer and the two monomeric A–B molecules is:

$$\Delta E = (1-k_1)\alpha_1 - (1-k_2)\alpha_2.$$

Hence, when $k_1 = k_2 = 0$,

$$\Delta E = \alpha_1 - \alpha_2.$$

Thus the above analysis shows the possibility of complexes being formed without use of free orbitals due to polar interaction. We note that in this a complex from polar molecules acquires the properties of a covalent compound: the dipole moment of the complex equals zero, there is a molecular orbital envoloping all the nuclei, etc.

In this instance the part played by overlap is small, not because there is little overlap of the atomic bonding orbitals, but on account of the low electron density in these orbitals and because the increase in overlap due to the utilisation of more directed vacant orbitals changes nothing (the overlap of "empty" orbitals does not give bonds). A similar situation occurs in some organometallic compounds and also in the formation of intramolecular hydrogen bonds [2,19]. Accurate calculations [20,21] made for H_3^+ and B_2H_6 confirm the correctness of what has been stated for the formation of non-polar bridge bonds.

On the basis of the above, it can be stated that the bonding in electron-deficient compounds is due to: (1) the delocalisation of electrons in the formation of polycentric orbitals with the utilisation of the free orbitals of the metal atom, or (2) strong polar interaction in the formation of structures with alternating charges of different polarity; polycentric orbitals can be formed here without utilisation of the free orbitals of the metal atom.

II. WHAT IS UNDERSTOOD BY THE EXPRESSIONS "ENERGETICALLY FAVOURABLE ORBITAL" AND "UTILISATION OF VACANT ORBITALS"

In speaking about "energetically favourable free orbital" we mean that the energy for the promotion of an electron in a valence state is moderate and can be restored in the formation of chemical bonds of the given atom with others. The use of this definite orbital ("free orbital") signifies that in it there is some electron density, that is, the most favourable polycentric molecular orbitals are obtained when this particular free orbital takes part in their formation. In the MO LCAO language this signifies that when a molecular orbital can be written in the form $\psi_M = \sum_k a_k \psi_k$, then the coefficient in the "favourable" orbital is not zero.

Often no mention is made in the literature of what is understood by these expressions [6,7,22]. For example, Hoffmann [23] considers that when the free $3p$ orbital of aluminium is used in compounds of the $[Al(C_2H_5)_3]_2$ type, the CH_2 bridging group should be in weaker fields than the terminal, since then the electrons of atom C will be distributed in two aluminium orbitals. This statement signifies that some charge is transferred from the CH_2 bridging group to the "favourable" orbitals of the aluminium atoms. However, this would be correct were it to be shown that in using the free orbitals of the aluminium atom there is a "flowing in" of charge into its free orbitals from other atoms or atomic groups, but the use of these free orbitals by the electrons of the aluminium atom for the purpose of creating more directed orbitals is unfavourable. Such an analysis has not been made. The reverse effect occurs in boron hydrides. With diborane [24] the bridging protons are in stronger fields than the terminal protons, that is, charge is transferred from the boron to the bridging protons, however, it is thought that in the formation of polycentric molecular orbitals the free p orbitals of a boron atom are used. That being so the free orbitals of the atom are used by "its own" electrons.

One of the fundamental problems in the study of bonds in electron-deficient compounds is that of the participation of the free orbitals of the metal atom in the formation of the polycentric molecular orbitals.

In the subsequent discussion of NMR results attention will be drawn to the experiments which confirm the use of free p orbitals of boron, aluminium, and lithium atoms.

III. NMR SPECTRA OF BORON HYDRIDES

There have been many detailed articles [1,25] about the investigation of the structure and properties of the boron hydrides, therefore we will limit the discussion to only the NMR results obtained for these compounds.

The study of the boron hydrides by the NMR method began as soon as their most important peculiarities had been revealed. However, the use of the NMR method gave more than confirmation of the results obtained earlier.

1. Proton Magnetic Resonance (PMR) Spectra

The PMR spectra of the boron hydrides are very complex owing to splitting, which is connected with the interaction of the protons with the ^{11}B and ^{10}B nuclei. As an

example, Fig. 1 gives the PMR spectra of diborane, pentaborane, and decaborane. The asymmetric form of the PMR spectrum for diborane rules out the possibility of an "ethane-like" structure existing.

When the method of double nuclear resonance is used a simplified spectrum is obtained [26]. Esentially, in addition to the high-frequency field bringing about the transition of the ^1H nucleus, a strong field, corresponding to the frequency of the transitions of the ^{11}B nucleus is imposed. This leads to saturation of the ^{11}B signals. At saturation the ^{11}B nucleus appears to cease to interact with protons and the splitting due to the $^{11}B-^1H$ interaction ceases. Fig. 2 shows the PMR spectra of the same compounds as in Fig. 1 obtained by the double resonance method.

The diborane spectrum shows the presence of two types of protons. The ratio of the intensities of the signals suggests that one group consists of two hydrogen atoms, and the other of four. This confirms the "bridge" structure of diborane.

The molecule of pentaborane, B_5H_9, has a tetragonal pyramidal structure [27]. The boron atom situated at the apex of the pyramid is combined with one proton and each boron atom lying at the base of the pyramid is linked with one terminal hydrogen atom and two bridging hydrogen atoms. The NMR spectrum should in principle give three groups of lines with 1:4:4 ratio of intensities. The PMR spectrum observed experimentally (Fig. 1*b*) consists of four

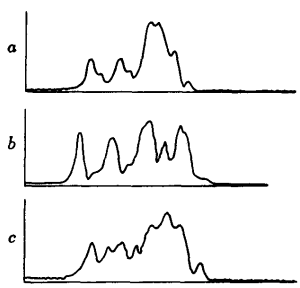


Fig. 1. PMR spectra of boron hydrides [24] (f_{res} = 30 MHz): *a*) diborane; *b*) pentaborane-9; *c*) decaborane.

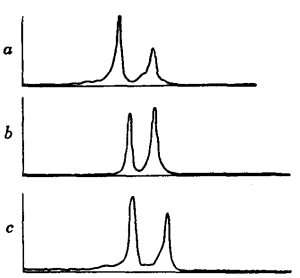


Fig. 2. PMR spectra of boron hydrides (f_{res} = 30 MHz) obtained on saturation of ^{11}B at the frequency 9.65257 MHz: *a*) diborane; *b*) pentaborane; *c*) decaborane.

intense lines (the signal of the terminal protons, bound to the boron atoms at the base of the pyramid, split owing to interaction with ^{11}B), four weak lines, somewhat displaced into the region of stronger fields (the line from the proton at the apex of the pyramid is split because of interaction with ^{11}B) and finally a group of lines from bridging protons, which is superimposed on the spectrum of the terminal protons. By using the double resonance method, on saturating the ^{11}B nuclei lying in the base a spectrum consisting of two lines of different intensities is observed. This indicates that the number of terminal and bridging protons connected with the boron atoms in the base of the pyramid are the same. In saturation of the ^{11}B "vertex" nucleus a signal from the proton bound to it is observed; the signal is positioned between the signals from the terminal and bridging protons lying in the base of the pyramid.

The PMR spectra of pentaborane-11, decaborane, etc. have been described in detail [28-33]. The analysis of the spectra confirmed the earlier findings concerning the peculiarities of the structure of these compounds.

The PMR spectra were obtained for the pure compounds and not solutions, external standards were not used, and in the overwhelming majority of the instances the spectra were not calibrated. The internal chemical shift was measured for diborane: the NMR bridging protons are shifted into the strong field region by 4.3×10^{-6} relative to the terminal protons. This suggests that the negative charge on the bridging protons is greater than that on the terminal, and when terminal B–H bonds are considered close to covalent bonds then the bridging bonds have a significant percentage of ionicity. Actually by using the wave functions of diborane obtained by Jamadjaki [21] it is easy to show that the excess of negative charge on the bridging proton compared with the terminal is $\sim 0.25\ e$. On each of the boron atoms there is a positive charge of $\sim +0.24\ e$. It is evident that such a charge distribution corresponds to the model of Pitzer and Gutowsky [2] which explains the bond by the formation of a B–B "protonated double bond", since the appearance of a signal from the bridging protons in weak fields would then be expected.

Kern and Lipscomb [34] made an approximate calculation of the magnetic screening for bridging and terminal protons in diborane and obtained qualitative agreement with the experimental results. They showed that the bridging protons are situated in strong fields and the internal chemical shift was found to be 3.2×10^{-6}.

2. ^{11}B NMR Spectra

The NMR spectra of the boron hydrides showed the presence of non-equivalent nuclei of ^{11}B and protons and gave additional confirmation of the correctness of the structures found by other methods.

The ^{11}B NMR spectrum of diborane consists of nine lines [24] (Fig. 3). Due to the strong interaction with the terminal protons the ^{11}B lines give a triplet $J_{^{11}B-^1H_K}$ = = 137 Hz), but the interaction with the bridging protons gives an additional triplet splitting of each of the three lines ($J_{^{11}B-H_M}$ = 48 Hz). Analysis of the spectrum confirms the non-equivalency of the two groups of protons and shows the equivalency of the boron nuclei.

The pentaborane-9 spectrum consists of two lines with intensity ratio $\simeq$ 4:1 (Fig. 4). The interaction of the boron atoms lying at the base of the pyramid with the

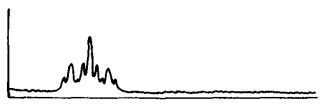


Fig. 3. ^{11}B NMR spectrum of diborane[24] (f_{res} = 12.3 MHz).

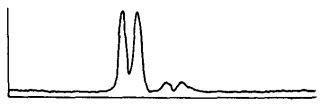


Fig. 4. ^{11}B NMR spectrum of pentaborane[24] (f_{res} = 12.3 MHz).

bridging protons is not shown clearly but the lines are appreciably broader than in diborane. Possibly one of the reasons for the broadening of the ^{11}B NMR lines is the interaction of the ^{11}B nucleus with the bridging proton.

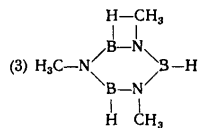
The ^{11}B NMR spectrum of other boron hydrides has been described in detail[30-33,35,36] and since the interpretation of the spectra is usually given for confirmation of their structure, we will restrict the discussion to diborane and pentaborane-9.

The study of ^{11}B NMR has been carried out more thoroughly than the NMR of the protons. We now have much information about the chemical shifts of ^{11}B and about the $^{11}B-^{1}H$ spin–spin interaction. Table 4 gives data on the chemical shifts and spin–spin interactions for some boron-containing compounds[36].

As Table 4 shows, the ^{11}B shift in diborane relative to $B(OCH_3)_3$ is very small. It can evidently be assumed that the boron atom in compounds such as $B(OCH_3)_3$, is "stripped".

However, such a hypothesis would not be correct for other boron compounds (for example, for diborane), since it has been noted that with change in the hybridisation of

TABLE 4.

Compound	$\delta=\frac{H_{specimen}-H_{std}}{H_{std}}\times 10^6$		$J_{^{11}B-^{1}H}$, Hz	
(1) $B(OCH_3)_3$	0			
(2) $B(OC_2H_5)_3$	+0.6			
(3) 	−14.3		134	
(4) $NaBH_4$	+61.0		81	
(5) B_2H_6	+0.5		137($H_{terminal}$) 48(H_{bridge})	
(6) B_4H_9	+25.0		132	
	+59.9		156	
	+30.8			
	base	apex	base	apex
(7) B_5H_9	+30.8	+69.6	168	176
(8) $B_{10}H_{14}$	+6.9	+53.9	124	159
	+19.5		128	
(9) B_6H_{11}	−16.2	+49.8	134	142
	+ 0.7		162	

the boron atom (on transition from sp^2 to sp^3) the paramagnetic contribution to the screening constant decreases[35,36].

Without evaluating the changes in the paramagnetic contribution it is impossible to draw any conclusions about the electron density at the ^{11}B nucleus.

The spin–spin constants of the $^{11}B-^{1}H$ interaction for the boron hydrides can be explained qualitatively on the basis of the hypothesis of Gutowsky and coworkers[37] that the spin–spin interaction between ^{1}H and other nuclei will depend on the fraction of s character in the hybrid orbital bound to the hydrogen atom. Hence the interaction constant between ^{1}H and the sp^2 hybridisation of the boron atom should be greater than that between ^{1}H and the sp^3 hybridised atom. The results in Table 4 confirm this hypothesis. Thus, for compound (3), in which the hybrid boron orbitals are close to sp^2, the quantity $J_{^{11}B-^{1}H}$ is 134 Hz, but for $NaBH_4$ where the hybridisation of the boron atom is close to sp^4, $J_{^{11}B-^{1}H}$ = 81 Hz.

When the spin–spin interaction constant $J_{^{11}B-^{1}H}$ reflects the influence of the s character of the hybrid orbitals of the boron atom, then the hybrid orbitals of the boron atom in hydrides are intermediate between sp^2 and sp^3. With diborane a difference in the hybridisation of the orbitals of the boron bound with the terminal and the bridging protons appears quite distinctly (137 and 48 Hz). In the last the contribution of p character is greater.

The information on spin–spin interaction shows that the B–H bonds (even bridging) are predominantly covalent. Were they strongly polar, then it is evident that the $J_{^{11}B-^{1}H}$ spin–spin interaction would be close to zero, as it is for $B(OCH_3)_3$.

3. Saturation of the ^{11}B NMR Signals

The ^{11}B nucleus is known to have a nuclear quadrupole moment, and the interaction of nuclear quadrupole with the "lattice" and with other nuclei diminishes[26] with the spin–lattice relaxation time T_1, and with the spin–spin relaxation time T_2. The optimal conditions for recording the spectra are short T_1 (since the signal intensity $\propto \sqrt{T_2/T_1}$) and long T_2 (since the signal decay $\propto 1/T_2$). The difference in the line breadths or their intensities can give some information about the electron environment of the ^{11}B nucleus.

Actually in many ^{11}B NMR spectra of boron hydrides the peak area of the NMR signals of the ^{11}B nuclei in non-equivalent positions give only approximately the number of nuclei found in the corresponding positions. The explanation is that the ^{11}B nuclei are in electronic surrounding with unusual symmetry and the interaction of the quadrupole moment ^{11}B with the electric field alters the spin–lattice relaxation time differently for nuclei situated in different positions. For example, the ^{11}B NMR signal of the BH_4^- ion is easily saturated (T_1 is large) and this is the result of the symmetry of the electronic environment of the ^{11}B nucleus, which decreases the interaction of the ^{11}B quadrupole moment with the lattice. The position for exchange is similar.

The study of "relative ease of saturation" for the boron hydrides gave the following results: the BH_2 groups in tetraborane-10 are saturated more readily than the BH groups[38]; the apex boron atom in pentaborane-9 is saturated more readily than the boron atoms lying at the base

of the pyramid, etc.[33,39]. In both instances the saturation at these nuclei is easier because of the high symmetry of the electron environment.

It was found for hexaborane-10 that the ^{11}B nuclei lying in the base are saturated much more easily than those at the vertices and this is difficult to explain by the presence of a symmetrical electron environment, due to the structure of the compound itself. Evidently this is brought about by the exchange of "bridging" hydrogen atoms, as the symmetry of the electron environment increases in similar intramolecular rearrangements. Exchange leads to the absence of $J_{^{11}B-H_M}$ spin–spin interaction noted earlier for pentaborane-9 and for other compounds[39].

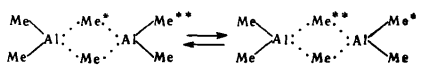
IV. NMR OF ORGANOALUMINIUM COMPOUNDS

Some organoaluminium compounds are electron-deficient. For example, there are the dimers of trimethylaluminium and triethylaluminium, the polymers of $Al(OPr^i)_3$, etc.[2,40].

The difference between the organoaluminium compounds and the boron compounds is that the polarity of the bonds can play a greater part in the formation of bridge bonds in them. Actually, in accordance with the electronegativity rules[15] the polarity of the C–Al bonds is ~ 30%. Furthermore, in the formation of polycentric orbitals with participation of the free 3*p* orbitals, the energy of the Al...C bridging bonds should be appreciably less than for B–H, since the energy for promoting in the valence state for the aluminium atom is greater than that for boron (see Table 2). And finally, in the formation of dimers by the alkylaluminiums steric hindrance to complex formation may arise[2].

1. PMR Spectra

It was established earlier that trimethylaluminium exists as a dimer in the solid state (its structure is shown in Table 1). In benzene solutions[2] and in the gaseous state[41] trimethylaluminium also exists as a dimer, but in early work on PMR, the spectrum of $[Al(CH_3)_3]_2$ appeared as a single line[26,42]. This can be explained either by the equivalence of all groups in the dimer, or by rapid exchange:


(I)

Miller and Pritchard[43] showed that at ordinary temperatures there is an exchange between bridging and terminal CH_3 groups. On cooling a solution of trimethylaluminium in cyclopentane to -75° a spectrum is obtained which consists of two lines with an intensity ratio of 2 : 1. The form of the spectrum is shown in Fig. 5. The shifts of the bridging and terminal methyl groups relative to the signal of cyclopentane are respectively 1.04×10^{-6} and 2.17×10^{-6}. At elevated temperatures the signal from the bridging groups broadened and merged with the signal from the terminal groups.

The activation energy for the transition mentioned, calculated from the temperature dependence of the form of the spectrum lay within the limits 6–14 kcal mole^{-1}. The heat of dissociation of the dimer[5] is 20.2 kcal mole^{-1}, and apparently trimethylaluminium does not dissociate into the monomer during change (I). It is thought[43] that the formation of a transitional state can rule out rupture of one

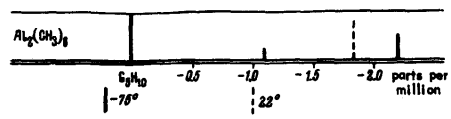
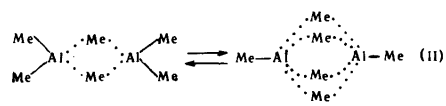


Fig. 5. PMR spectrum of the dimer of trimethylaluminium[44].

Al–C bond or the formation of new Al...C bonds for the transitional structure, that is,


(II)

Hyperfine splitting due to the $^{27}Al-^1H$ interaction was not observed.. The PMR lines are very broad (~ 6 Hz).

For dichlorotetramethyldialuminium $Al_2Cl_2(CH_3)_4$ the PMR lines have a breadth of ~ 1 Hz (f_{res} = 40 MHz), but here in the temperature interval -85–0° the $^{27}Al-^1H$ spin–spin interaction was not observed[44].

The absence of hyperfine splitting is easily explained by the great polarity of the C–Al bonds or by the fact that in the hybrid Al orbital the 3*s* state "impurity" is small.

The PMR spectrum of $[Al(C_2H_5)_3]_2$ shows that all the CH_2 groups are equivalent[23,45]. If the "usual" association were assumed, the non-equivalency of the CH_2 groups would be expected:

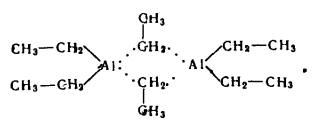
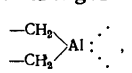
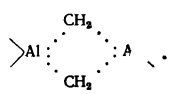


Fig. 6 shows the PMR spectrum. The methylene group signal appears at the "mean" value of the field: between the positions expected at a stronger field for



and the position for the bridging CH_2 gr' ups in the configuration:



Hoffmann considers[23] that the NMR signal of the bridging groups should be expected in a weaker field, since then the electrons of the C–Al bond will be distributed on two orbitals of the aluminium.

The hypothetical positions of the signals of the outer ethyl groups (or the bridging groups) can be judged from the spectra of compounds with –Al–CH_2– groups which

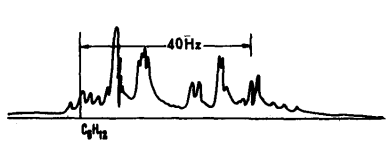
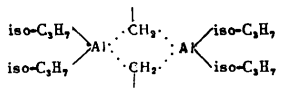


Fig. 6. PMR spectrum of the dimer of triethylaluminium[44] (f_{res} = 40 MHz).

either are not associated, for example[46], $AlPr^i_3$, or contain an ethyl group only in the bridge bond, for example,



For the CH_2 groups in these instances[23] a frequency difference of 17.6 Hz is obtained (at f_{res} = 40 MHz), in which the bridging methylene group gives a signal in weaker fields than the terminal groups. But because a single line is observed for triethylaluminium, it is thought[23] that here there is an alkyl exchange. Assuming that the shift between the terminal and bridging $-CH_2-$ groups should be ~ 17 Hz it can be concluded that the Al...C bridging bond is unstable and has a life of $\tau \ll 10^{-2}$ s.

However, the instability of the Al...C bonds cannot be considered to be finally established, since the NMR spectra at low temperatures have not been investigated (as they have for trimethylaluminium[43]), and there have also been no studies of the applicability of the "static" model, proposed earlier by Pitzer and Gutowsky[2] (bonding in the complex by the formation of Al...H bonds is suggested, as shown in Fig. 7). This model is reasonable from the standpoint of "geometry" and to explain the same position of the signals for the methylene groups there is no need to invoke the existence of exchange.

The data about the PMR spectra of other compounds (diethylaluminium hydride, etc.[23,44,45]) are fragmentary and will not be discussed here.

2. ^{27}Al NMR

The ^{27}Al nucleus has a comparatively large quadrupole moment ($Q = 0.149 \times 10^{-24}$ e cm^{-2}) and if its electronic environment does not have sufficient symmetry then owing to the interaction of the quadrupole moment with the electric field T_2 decreases and the aluminium line broadens. The ^{27}Al NMR usually is very broad but since the range of shifts for ^{27}Al is great not only the line breadth but also the chemical shifts can be measured with an accuracy of $\pm 10 \times 10^{-6}$. Some data[47] for the NMR of aluminium compounds are given in Table 5.

The spectra of the compounds mentioned in Table 5 were taken at a frequency of f_{res} = 7.2 MHz.

The narrow lines of the ^{27}Al NMR show compounds having electric field symmetry around the ^{27}Al nucleus close to the tetradhedral $Al(CH_3)_3$, $AlCl_3$, and solutions of the polymer $Al(OPr^i)_3$.

Pure trimethylaluminium gives a wider ^{27}Al NMR line than $AlCl_3$, and this can be explained by the dimer

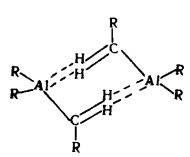


Fig. 7. Structure of the dimer of triethylaluminium according to Pitzer and Gutowsky[2].

TABLE 5.

Compound	$\delta = \frac{H_{specimen} - H_{std}}{H_{std}} \times 10^6$	Line breadth, G
$Al(N_2O)^{+3}_6$	0	0.05
$[Al(CH_3)_3]_2$	—156	0.4
$[Al(C_2H_5)_3]_2$	—171	1.5
$Al(iso\text{-}C_4H_9)_3$	—220	5.4
$Al(O—iso\text{-}C_4H_9)_3$ (Solution in heptane)	—7	0.09
$[AlCl_3]_2$	—91	0.3
$H—Al(iso\text{-}C_4H_9)_2$	—162	8.9

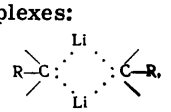
$[Al(CH_3)_3]_2$ being formed by the setting up of Al...H bonds[47], that is, a hydrogen atom of the methyl group, and not the carbon, takes part in the intermolecular bond. This is not in agreement with the X-ray data, but accords well with the Raman and infrared spectra[2] where it is found that the symmetry of $[AlCl_3]_2$ is higher than that of $[Al(CH_3)_3]_2$.

The dimer of triethylaluminium gives a relatively "narrow" line, evidently because the gradient of the electric field at the ^{27}Al nucleus diminishes on formation of the A...H bonds. Were exchange to exist, an NMR line almost coinciding in breadth with the trimethylaluminium line would be expected. For the molecule-monomers, for example, $AlPr^i_3$, the symmetry of the electronic environment of the ^{27}Al nucleus is lower and the line becomes significantly wider.

The chemical shifts of the compounds discussed have not been interpreted.

V. NMR OF ORGANOLITHIUM COMPOUNDS

It has been found[4] that organolithium compounds are strongly associated, and with ethyllithium even in the vapour the molecules exist predominantly in the form of tetramers and hexamers[48]. The considerably branched molecule of $(CH_3)_3CLi$ gives tetramer complexes in benzene solution[49]. The simplest dimer associate was found in an ethereal solution of phenyllithium[50]. However, not one of the papers we have read reports the observation of monomeric molecules of organolithium compounds. It is suggested[2,50] that the intermolecular bonds in the complexes arise because of the strong polarity of the C–Li bonds. From the infrared spectra[51] and the chemical properties of the substances (solubility in non-polar solvents, electrical conductivity, etc.) its was proposed that multicentric molecular orbitals and C...Li bridge bonds are formed in the organolithium complexes:



and the 2p orbitals of the lithium atom participate in the formation of the multicentric orbitals. The proposed C...Li bonds are essentially covalent.

The difference between the lithium atom and the atoms of boron and aluminium is that the 2p orbitals of the lithium atom are not used in the normal state (and therefore information about the participation of any of the 2p orbitals in bonds is needed for the solution of problems). In addition allowance must be made for polarity of the bonds playing an important part in the formation of complexes.

1. PMR Spectra

Table 6 gives some information about the PMR spectra of some organolithium compounds.

Figs. 8–10 show PMR spectra of methyl-, ethyl-, and phenyl-lithium.

The results for the chemical shifts of PMR for the CH_2 group cannot be explained in terms of electronegativity by the rules found earlier for alkylmetals [54]. The large shift of the CH_2 line in the region of strong fields can be explained if it is assumed that the C–Li bond is strongly polar. In reality the shift of the CH_2 group in $(R-Li)_n$ complexes relative to the CH_2 group in normal hydrocarbons is [26] $\sim 2.6 \times 10^{-6}$. To obtain such a shift the charge on the 1s cloud of the hydrogen atom must be increased by 0.2 *e*. When it is assumed that the charge is transferred from the lithium atom to the CH_2 group and there distributed in accordance with the electronegativity of the atoms, then there should be a charge of $\sim 0.7\ e$ on the CH_2 group.

The NMR results for alkyl compounds of normal structure show that outside the dependence on the complexity of the complex, the CH_2 group directly bound with the lithium atom is always found in the same electronic environment, although for different complexes some differences could be expected. For example, for the tetramer and hexamer of ethyllithium structures in the form of "bookcases" [layers (Ed. of Translation)] of dimers joined by C...Li bonds have been suggested [55] and also the structures [4] shown in Fig. 11. However, with the "bookcases" for the hexamer there should be a difference in the shifts of the CH_2 groups for different "layers" of the bookcase. Probably, for the structure proposed by Brown and coworkers [4] in the tetramer and hexamer there should be different electronic environments for the CH_2 groups.

When alkyl exchange is not taken into account the structures proposed above do not explain the PMR results, besides which these structures are highly stressed due to the mutual repulsion of the non-valence bonded atoms [52], which was noted earlier for the example of the triethylaluminium complexes [2]. Evidently as for $[Al(C_2H_5)_3]_2$ complexes [2], C_2H_5Li can exist in solution thanks to the formation of Li...H bonds [52] (Fig. 12). Such a structure also exists for the hexamer.

The size of the chemical shift of the CH_2 group, as for other structures is readily explained by the high polarity of the C...Li bond. The equivalence of the methylene groups is also evident, since the Li...H bonds are identical. The

TABLE 6*.

Substance	Solvent	Concentration, *N*	Association factor	$\delta = \frac{H_{specimen} - H_{C_6H_6}}{H_{C_6H_6}} \times 10^6$
CH_3Li	$(C_2H_5)_2O$	0.6—0.8		9.05±0.05
C_2H_5Li [4,82]	C_6H_6		6	8.11±0.05
	C_6H_{12}	0.5—0.8		8.11±0.08
	$(C_2H_5)_2O$	0.85—2.40		8.10
$n\text{-}C_4H_9Li$ [52]	C_6H_{14}	0.6—1.18		8.10
$C_{12}H_{25}Li$ [82]	C_6H_6	0.6		8.10
	C_6H_{12}	0.6		8.10
C_6H_5Li [80,83]	$(C_2H_5)_2O$		2	shift of the most intense line relative to benzene is 0.2
$t\text{-}C_4H_9Li$ [49]			4	6.16 (δ_{CH_3})

* $J_{^1H^7Li} \simeq 0$.

Fig. 8. PMR spectra of methyllithium in diethyl ether: *a*) lines of the CH_2 group of the ether; *b*) lines of the CH_3 group of the ether; *c*) lines of the CH_3 group of methyllithium (breadth $\simeq$ 1.4 Hz, f_{res} = 22.68 MHz).

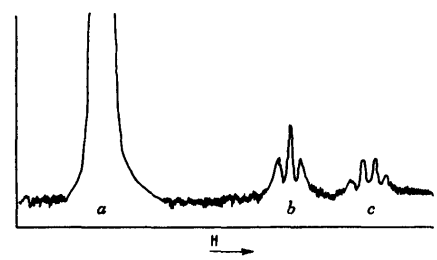


Fig. 9. PMR spectrum of ethyllithium in benzene (f_{res} = = 25 MHz):
a) benzene line; *b*) CH_3 group of ethyllithium; *c*) CH_2 group of ethyllithium.

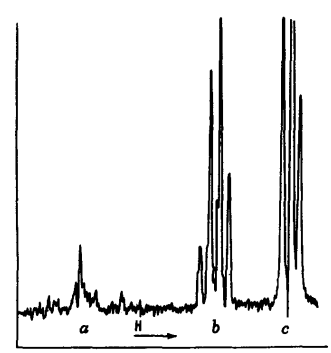


Fig. 10. PMR spectrum of phenyllithium in diethyl ether [53] (f_{res} = 25 MHz):
a) phenyllithium lines; *b*) CH_2 group of the ether; *c*) CH_3 group of the ether.

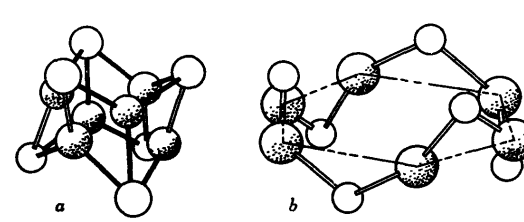


Fig. 11. Structure of the ethyllithium hexamer [4] (lithium atoms omitted). The alkyl exchange between the structures (*a*), postulated to explain the breadth of the ^7Li lines, is suggested as possible because of the formation of intermediate structures (*b*).

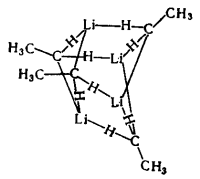


Fig. 12. Hypothetical structure of the tetramer of ethyllithium [52].

Li...H bonds are preferentially polarised bonds in which there is apparently some overlap of the 1*s* orbitals of the hydrogen atom with the 2*s* orbitals of the lithium atom. A feature of these bonds is that the free 2*s* orbital of the hydrogen atom agrees in energy [14] with the free 2*p* orbital of the lithium atom and on transfer of the 2*s* electron of the lithium atom to the 2*p* level, the electron can use the 2*s* orbitals of neighbouring hydrogen atoms without expenditure of energy [52].

The chemical shifts of the PMR lines for $(CH_3)_3CLi$ and C_6H_5Li were not interpreted.

All authors note the absence of $^7Li-^1H$ spin–spin interaction. This is associated either with alkyl exchange or with the great polarity of the C–Li bond (the latter is the more probable).

X-Ray analysis [55] of crystalline C_2H_5Li showed that the ethyllithium molecules form tetramers in the crystals. Apparently the dissolution of ethyllithium in non-polar solvents is due to the comparatively slight interaction of the tetramers with one another. The retention of the form of the tetramer in solution should give different shifts for the NMR lines of the methylene group protons. It can therefore be assumed that the complex changes its configuration to some extent during dissolution.

2. ^7Li NMR Spectra

The ^7Li nucleus has a quadrupole moment ($Q = 4.2 \times \times 10^{-26}$ *e* cm^{-2}) and therefore the breadth of the ^7Li line can be considerable owing to the interaction of the quadrupole moment with the "lattice". However, the ^7Li NMR lines of solutions of a series of compounds give narrow lines. Some of the NMR results are given in Table 7.

Brown and coworkers [4] explain the narrow ^7Li NMR lines by the exchange of radicals as for trimethylaluminium [43]. However, the line breadth is unaltered on cooling to -75° (and ether solutions to -100°) therefore it can be assumed that the narrow ^7Li line is due to the symmetry of the electron environment and not to exchange. Actually if it is assumed that the structure shown in Fig. 12 is stable, then the absence of electric field gradients at the ^7Li nucleus is the result of the compensating action of the neighbouring H, C, and Li atoms.

TABLE 7.

Substance	Solvent	ΔH_{Li}, Hz (t = 27°)	ΔH_{Li}, Hz (t = −75°)
C_3N_3Li [4]	C_6H_6	$\sim 10^{-3}$	
C_2H_5Li [5]	C_6H_6	$<6\cdot10^{-3}$	
	C_6H_{12}	$<6\cdot10^{-3}$	
	$(C_2H_5)_2O$	$<6\cdot10^{-3}$	$<6\cdot10^{-3}$
$n\text{-}C_4H_9Li$ [52]	C_6H_{14}	$<6\cdot10^{-3}$	$<6\cdot10^{-3}$
$C_{12}H_{25}Li$ [52]	C_6H_6	$<6\cdot10^{-3}$	
	C_6H_{12}	$<6\cdot10^{-3}$	
$C_6H_5.CH_2Li$ [53]	$(C_2H_5)_2O$	$<6\cdot10^{-3}$	$<6\cdot10^{-3}$

We note that the strongly polar C–Li and Li...H bonds will give a narrow ^7Li NMR line for almost any configuration of the complex. The alkyl exchange postulated for the explanation of the small line breadths [4] of ^7Li lines apparently does not occur, since even at low temperatures a narrow line is observed. It is especially difficult to admit the possibility of exchange for such compounds as dodecyllithium.

Apparently in these compounds the ^7Li nucleus is almost in an environment of 1*s* electrons, that is, the C–Li and Li...H bonds are strongly polar.

This hypothesis is supported by comparison with the NMR results [47] for ^{27}Al. When it is assumed that for compounds of the $(Li-R)_n$ type in solutions the correlation time, viscosity, etc. are just the same as for $[Al(CH_3)_3]_2$ (which is probably not true, as there are changes in the direction of the broadening of the ^7Li line) then the ratio of the line breadths should determine the ratios of the squares of the quadrupole moments [56] and the ^7Li NMR lines should have a breadth of more than 2×10^{-1} Hz. Comparison with the experimentally observed line breadths allows the conclusion to be drawn that the ^7Li nucleus has an electronic environment of high symmetry. Evidently there is very little utilisation of free orbitals and the lithium in these compounds is in a form close to Li^+. This suggestion explains the PMR results, the line breadths, and the absence of spin–spin interaction.

The chemical shifts in ^7Li were observed in only one work [4], but definite conclusions were not drawn, since the standard was a solution of lithium bromide in water. The shift of $\sim 1 \times 10^{-6}$ of the lithium lines (ethyllithium) towards weaker fields relative to lithium bromide does not seem significant since the transfer of electrons from the water molecule to the free orbitals of Li^+ is possible (in the formation of a hydrated ion).

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The examples considered show that the bonds in organo--lithium, -aluminium, and -boron complexes differ considerably: from close to covalent to strongly polar bonds. Therefore to formulate the principles of electron-deficient bonding it is necessary to consider both polar interaction and also the possibility of using free orbitals. The principle formulated by Rundle [6,7] does not take polar interactions into account.

It is interesting to note that at first glance allowance for polar interactions can explain many experimental facts. For example, Pitzer and Gutowsky [2] suggested that when the bonds in the alkylaluminium dimers are predominantly polar then all the alkylmetals in which the metal atoms have less electronegativity are associated and those with greater electronegativity are monomers. This suggestion is equivalent to saying that M–C bonds for metals of low electronegativity are strongly polar. Such a compound will give complexes with formation of polar bonds, spin–spin interaction in these complexes will be absent, and the chemical shift of M relative to the M^+ ion will be small. In metals with high electronegativity the C–M bond will be predominantly covalent, there will be spin–spin interaction, etc. Cryoscopic and NMR data confirm this hypothesis.

TABLE 8.

Compound	Electronegativity of the M atom (Ref. 15)	Association factor	J_{M-CH_3}, Hz	J_{M-CH_3}, Hz
$C_2H_5{}^7Li$	0.95	6	0	0
$(CH_3)_3{}^{27}Al$	1.5	2[5]	0	0
$(C_2H_5)_3{}^{27}Al$	1.5	2[5]	0	0
$(CH_3)_3Ga$	1.6	unstable dimer[57]	—	—
$(CH_3)_3In$	1.7	1[6]	—	—
$(CH_3)_2{}^{111}Cd$	1.7	1		50.2±0.4[58]
$(C_2H_5)_2{}^{111}Cd$	1.7	1	49.4±0.8 51.2±0.8	59.8±0.8 57.2±0.8
$(CH_3)_2{}^{199}Hg$	1.8	1	—	102[59]
$(C_2H_5)_2{}^{199}Hg$	1.8	1	120 115.2	91[59] 87.6[60]
$(C_2H_5)_4{}^{207}Pb$	1.8	1	125.0	41.0[60]
$(CH_3)_4{}^{119}Sn$	1.9	1	—	54.2±0.3[58] 51.9±0.3
$(C_2H_5)_4{}^{119}Sn$	1.9	1	51.4±0.8 49.1±0.8	69.8±0.8 66.8±0.8
$(CH_3)_2{}^{125}Te$	2.1		20.7[61]	
$(C_2H_5)_2{}^{125}Te$	2.1		exists, but the spectrum is complex and has not been interpreted[61]	
$(CH_3)_2{}^{77}Se$	2.4		—	11.2±0.3[58]
$(C_2H_5)_2{}^{77}Se$	2.4		<15	15

Table 8 gives some cryoscopic and NMR results for various groups of organometallic compounds.

Pitzer and Gutowsky's views are also confirmed for alkylmetal complexes.

As for boron hydrides, it is almost impossible to confirm the use of all the 2*p* orbitals in the formation of bonds, but quantum mechanical calculations show the correctness of this hypothesis.

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Karpov Chemical Scientific
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RUSSIAN CHEMICAL REVIEWS
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NIKOLAI NIKOLAEVICH SEMENOV

Dear Nikolai Nikolaevich,

The whole Soviet scientific community, all chemists in our great Motherland warmly greet and congratulate you on the day of your glorious anniversary.

Your fundamental discoveries in the fields of chain reactions, of combustion, and of explosive processes have deservedly brought you world-wide recognition.

You won the deep gratitude of the Soviet peoples as an untiring propagandist for and organiser of science. Throughout your brilliant life you have been a convinced and staunch champion of the unity of theory and practice.

It is gratifying to realise that you come to your jubilee in the prime of your creative powers and your untiring talent for scientific organisation.

Together with all Soviet scientists the Editorial Board of the journal "Uspekhi Khimii" sends you its greetings and most sincere wishes for health and ever new successes in your many-sided activities.

U. D. C. 541.124.7

STUDY OF THE KINETICS AND MECHANISM OF BRANCHED CHAIN REACTIONS IN THE GAS PHASE

A. B. Nalbandyan

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I. INTRODUCTION

The present Review gives a brief account of the principal results obtained in investigations, conducted mainly at the Institute of Chemical Physics of the USSR Academy of Sciences during the past five to six years, in the field of branched chain reactions, the theory of which has been developed by Semenov. Thanks to the powerful research tools which have appeared comparatively recently — electron spin resonance (e.s.r.), electronic computers, etc. — it has become possible to undertake a broad testing of the mechanisms which have been suggested for complex chemical processes and to study new systems in which, with rare exceptions, it had not been possible to establish the nature of the active species responsible for the development of the chain processes.

Forty years ago Semenov and his students at the Leningrad Physicotechnical Institute, in a study of the quenching of the luminescence of the combustion products from a mixture of phosphorus vapour and oxygen, observed the remarkable phenomenon of lower and upper limits of spontaneous combustion. During 1926–1930 the phenomenon of ignition limits was discovered also in sulphur vapour–oxygen, carbon monoxide–oxygen, and hydrogen–oxygen mixtures[1-8]. Investigations showed that practically no reaction took place below the lower or above the upper limit. It was sufficient, however, to raise slightly the pressure of the mixture near the lower limit, or lower it when above the upper limit, for the mixture to ignite instantly. The investigators noticed that the lower and upper limits possessed unusual properties. For example, the lower pressure limit is lowered by increasing the diameter of the vessel. Under identical conditions, dilution of the reactant mixture with an inert gas results in a fall in the limiting pressure of the combustible mixture. In other words, a mixture which does not inflame at a given pressure immediately ignites if an inert gas is added to it. On the other hand, the partial pressure of the reactant mixture at the upper limit falls sharply if it is diluted with an inert gas. All these and many other phenomena discovered at the same time and later do not fit into the framework of classical chemical kinetics.

In order to explain these astonishing phenomena, Semenov[2-9] put forward a theory of chain branching in chemical reactions, according to which the combustion of a gaseous mixture involves the direct participation of atoms and free radicals, the so-called active centres or chain carriers. Atoms and radicals react with the starting materials to form the final product and a new active particle. The latter again reacts, to give the reaction product and an atom or a free radical as new active particle. In this way an unbranched chain reaction arises and is propagated in the gas mixture, a phenomenon known since the discovery of the photochemical chlorination of hydrogen by Bodenstein[10]. The ignition of fuel mixtures is due to the branching of chains, i.e. to the appearance from time to time, at some link or links in the developing chains, of more than one active particle. These additional active centres also become centres of new chains. As a result, an avalanche-like increase in the number of active centres occurs in the system after a brief interval, and hence also in the reaction velocity, which we perceive as ignition. Mathematical analysis of the growth in the number of active particles in the reactant mixture shows that in this case the increase obeys the law $N = N_0 e^{\varphi t}$, where φ is a positive quantity.

The lower and upper limits of spontaneous ignition observed experimentally by Semenov were explained by the destruction of active centres or chain carriers. According to Semenov's theory, the lower limit is associated with heterogeneous destruction of chains, and the upper limit with their homogeneous destruction. This theory provided a quantitative description of the experimentally observed ignition limits and their properties.

According to the theory of the limits, absence of ignition is explained by the rate of destruction of active centres on the walls or in space exceeding the rate of branching. Ignition occurs only when the rate of branching of chains is greater than the rate of destruction of active centres. The lower ignition limit is determined by equality of rates of branching and of heterogeneous destruction of active centres, and the upper limit by equality of the rates of branching and of homogeneous destruction of chain carriers. The experimentally observed decrease in the lower pressure limit with increase in diameter of the reaction vessel and with dilution of the mixture by an inert gas are brilliantly explained by Semenov's theory of the limits. With a reaction vessel of larger diameters, the average time taken by an active particle to diffuse to the walls of the vessel is longer, and consequently the probability is higher of its entering into new branching reactions before destruction on the walls. Additions of an inert gas should act similarly to an increase in pressure. With dilution of the reactant mixture, the mean residence time of an active centre in free volume increases, since diffusion is slower. The decrease in the partial pressure of the reactant mixture at the second limit and the second limit itself are well and quantitatively explained by the theory of branched chain processes on the assumption that in space an active centre is destroyed in a three-body collision[9,11], while the branching reaction is bimolecular. The rate of branching will then increase in proportion to the pressure of the reactant gas, while the rate of termination will increase according to the square of the pressure. With rise in pressure, these rates can obviously become equal when the pressure reaches a certain value, and above this pressure the mixture will cease to ignite. When part of the reactant gas is replaced by an inert gas, the number of three-body collisions remains constant, while the rate of branching falls. For this reason ignition ceases at a lower partial pressure of the reactant gases as the pressure is raised.

Semenov's theory of branched chain processes very soon obtained world-wide acceptance. An immense number of papers appeared, in which numerous examples were given of reactions occurring by a branched chain mechanism. It became evident that chain reactions are not rare exceptions. An urgent need therefore arose for a detailed study of the kinetics and mechanism of chain processes. It was obvious that the conscious control of a chemical process was indissolubly linked with a knowledge of the detailed mechanisms of actual chain reactions. Thus in 1930 a second important period began of further development and testing of the theory of chain reactions. In the study of the mechanism of complex chemical processes, each comprising the aggregate of a series of elementary reactions of atoms and free radicals with the starting materials and intermediate products, the question first arises of the nature and reactivity of the active particles responsible for development of the process.

At the outset of the development of the theory of branched chain reactions, the combustion of hydrogen provided the

example on which a quantitative check of the theory came to be made. This reaction, while being less complicated than others, nevertheless possessed many features in common with other complex reactions.

As a result of the great efforts made by investigators in various countries, the following most probable mechanism became generally accepted for the combustion of hydrogen at pressures not exceeding atmospheric

$$H_2+O_2 \rightarrow 2OH, \quad (0)$$

$$OH+H_2 \rightarrow H_2O+H, \quad (1)$$

$$H+O_2 \rightarrow OH+O, \quad (2)$$

$$O+H_2 \rightarrow OH+H, \quad (3)$$

$$H \xrightarrow{walls} {}^1/_2 H_2, \quad (4)$$

$$O \xrightarrow{walls} {}^1/_2 O_2, \quad (5)$$

$$H+O_2+M \rightarrow HO_2+M, \quad (6)$$

$$OH \xrightarrow{walls} {}^1/_2 H_2O_2. \quad (7)$$

It is assumed in this scheme that hydrogen and oxygen atoms and the hydroxyl radical are the active centres responsible for chain propagation and branching in mixtures of hydrogen and oxygen, i.e. for reactions (1)–(3).

Much was done by workers to prove that these active species were involved in the combustion of hydrogen. Indirect evidence of their important role is provided by experiments on the action of hydrogen and oxygen atoms on the range of ignition of hydrogen–oxygen mixtures and on the length of the induction periods preceding ignition.

It was shown in the Institute of Chemical Physics of the USSR Academy of Sciences that the effect of hydrogen atoms is to raise the upper limit of spontaneous ignition, while the range of ignition is displaced to lower temperatures [12]. The action of oxygen atoms is far stronger. In the presence of high concentrations of oxygen atoms, produced in an electric discharge, an upper limit cannot be detected. The ignition temperature of the reactant mixture falls from 400°C to room temperature [13]. It was also established [14] that the induction period preceding ignition is markedly shortened under the influence of hydrogen and oxygen atoms.

A great success of the theory of branched chain reactions was provided by the direct experimental proof of the formation of high concentrations of hydroxy-radicals in low-pressure flames of hydrogen with oxygen. Using the method of line absorption spectroscopy [15], Kondrat'ev and his collaborators [16–18] showed that, in a low-pressure hydrogen–oxygen flame at pressures somewhat exceeding that at the lower limit, the concentration of hydroxy-radicals is several thousand times as great as the equilibrium value under the conditions of the flame. Avramenko's investigations [18] showed that the reaction velocity, determined from the quantity of water formed, varies linearly with the total concentration of hydroxy-radicals.

Experimental results obtained in this work were used to determine the rate constant of reaction (1), which was

$$k_1 = 7\times10^{-12}\sqrt{T}\,e^{-\frac{10\,000}{RT}} \text{ cm}^3\,\text{s}^{-1}\,\text{mol.}^{-1},$$

Semenov [19] estimated the rate constant k_2 of the branching reaction (2) from Koval'skii's data [20]. Its activation energy was close to 18 kcal. The activation energy of reaction (3) was estimated as 6 kcal from experimental data obtained by Harteck and Kopsch [21] for two temperatures in a study of the interaction of atomic oxygen with hydrogen. The latest, more accurate data of Azatyan et al. [22] give values for the rate constants of the elementary reactions (2) and (3) of respectively

$$k_2 = 1.3\times10^{-10}e^{-\frac{16\,900}{RT}} \text{ cm}^3\,\text{s}^{-1}\,\text{mol.}^{-1}$$

$$k_3 = 1.1\times10^{-10}e^{-\frac{11\,700}{RT}} \text{ cm}^3\cdot\text{s}^{-1}\,\text{mol.}^{-1}.$$

According to the scheme given above for the combustion of hydrogen, the rates of reactions (1)–(3) are respectively

$$w_1 = k_1[OH][H_2];\ w_2 = k_2[H][O_2];\ w_3 = k_3[O][H_2].$$

For one intermediate temperature near which investigations are usually made, e.g. for $T = 600°$, the ratios of the rate constants can be written in the form

$$k_1[H_2]:k_2[O_2]:k_3[H_2] = \frac{k_1[H_2]}{k_2[O_2]}:1:\frac{k_3[H_2]}{k_2[O_2]} = 46\frac{(H_2)}{(O_2)}:1:7.6\frac{(H_2)}{(O_2)}.$$

For hydrogen-rich mixtures, e.g.

$$[H_2]:[O_2] = 9:1\quad k_1[H_2]:k_2[O_2]:k_3[H_2] = 415:1:68.$$

This means that the inequality

$$k_2[O_2] \ll k_3[H_2] \ll k_1[H_2]$$

should hold in very hydrogen-rich mixtures with oxygen.

The reciprocals of the rate constants

$$\frac{1}{k_1[H_2]};\quad \frac{1}{k_2[O_2]}, \text{ and } \frac{1}{k_3(H_2)},$$

measure the life of the corresponding active centres from the moment at which they appear until they undergo fresh reactions. Hence $t_H \gg t_O \gg t_{OH}$, where t is the life of the corresponding active species. From this inequality it follows that, in very hydrogen-rich mixtures, the concentration of hydrogen atoms should considerably exceed those of oxygen atoms and hydroxy-radicals. In an equimolecular mixture [H] > [O] > [OH]. In an $[H_2]:[O_2] = 1:9$ mixture, [O] > [H] > [OH].

Assuming the above mechanism as a basis, Semenov [23,24] studied in 1943 the kinetics of the burning of hydrogen-rich mixtures with oxygen at pressures somewhat exceeding that at the lower limit of spontaneous ignition. The investigations showed that under these conditions only the variation in the concentration of hydrogen atoms and their destruction on the walls of the reaction vessel need be taken into account. Changes with time in the concentrations of oxygen atoms and hydroxy-radicals can be neglected, since their concentrations are far lower than that of the hydrogen atoms. Simultaneous solution of the equations for time variation in the concentrations of atomic hydrogen and of one of the starting materials — oxygen — led Semenov to the important conclusion that large quantities of hydrogen atoms are formed in a low-pressure flame, the relative concentration of which may in some cases reach more than 20% of the initial hydrogen.

This cardinal conclusion of the theory was confirmed by experiments made by Kondrat'eva and Kondrat'ev [25], who used a thermoelectric probe method to detect hydrogen atoms and measure their concentration. Two fine thermocouples in very narrow thin-walled quartz sheaths were placed in a stationary low-pressure flame obtained under flow conditions. On the tip of the sheath of the first thermocouple was deposited a layer of $ZnOCr_2O_3$, a substance on which hydrogen atoms recombine at every collision. The tip of the second thermocouple was washed

with nitric acid, in order to minimise the recombination of atoms striking the surface. This thermocouple served to measure the flame temperature. These workers recorded temperature differences in the flame reaching under certain conditions 300 deg. This difference was obviously associated with the heat of reaction of atoms and radicals vigorously recombining on the surface of the thermocouple coated with $ZnOCr_2O_3$. From the equation which they deduced to link ΔT with the relative concentration ξ of hydrogen atoms, Kondrat'eva and Kondrat'ev obtained ξ = = 0.45. This value agrees very well with ξ = 0.51 calculated by means of Semenov's formula. It followed from the excellent agreement between the theoretical conclusions and experiment that, in very hydrogen-rich mixtures with oxygen, the lower ignition limit should be determined mainly by the two reactions of atomic hydrogen — the branching reaction $H + O_2 \rightarrow OH + O$ (2) and the loss of hydrogen atoms on the walls of the reaction vessel (4) — for the loss of oxygen atoms and hydroxy-radicals on the walls can be neglected under these conditions.

After 1930 it was increasingly remarked that the lower limit of spontaneous ignition depends not only on the diameter of the reaction vessel and on inert additions but also on the surface state and nature of the material of the reaction vessel[26-30]. This was allowed for in the theory of the lower limit by introducing a new parameter ϵ, the coefficient of recombination of active particles on the surface[31-33]. Variation in ϵ with surface state and material could be explained by the experimentally observed hundredfold variation in the pressure at the lower limit. At the same time several communications appeared in the literature[34,35] on the very strong action on the lower limit of thin metallic rods placed coaxially in the reaction space. The theory of this phenomenon was given by Semenov[33], who, on the hypothesis of an intense destruction of active centres on the surface of the thin rods, obtained an equation enabling the coefficient of recombination of the active centres to be linked with the lower limit and the diameters of reaction vessel and rod. The action of the thin rods on the lower limit of a stoichiometric mixture of hydrogen and oxygen was used[36] to determine the recombination coefficients of the active species. For this purpose thin rods ($d \simeq 0.1$ cm) of various substances were introduced by means of a movable electromagnet into a reaction vessel which had first been treated with $K_2B_4O_7$ (a substance on which recombination of hydrogen atoms is very poor), and the lower limits were determined in the absence and in the presence of the rods. The apparatus used is shown diagrammatically in Fig. 1. The ignition limit in these experiments was determined by rapidly admitting the mixture from the subsidiary volume B into the reaction vessel A. The rods were introduced and withdrawn by means of the movable electromagnet.

The results in Table 1 for a vessel having d = 1.83 cm show that the lower limit is raised to the greatest extent in the presence of rods coated with $ZnOCr_2O_3$ and made of graphite. The experimental data in Table 1 and the corresponding equations deduced on the basis of Semenov's theory were used to calculate the recombination coefficients ϵ of active particles on the surfaces investigated. The calculated results in Table 2 show that, depending on the material and state of the surface, the recombination coefficient may vary by factors of 10^4. The substances investigated can be arranged in a sequence according to their activity towards the recombination of active particles. The first place in this sequence is occupied by $ZnOCr_2O_3$ and graphite, which are followed by gold, platinum, tungsten, stainless steel, quartz which has been washed with HF solution, and finally Pyrex which has been treated with HF solution. In 1924 Bonhoeffer[37] studied the recombination of atomic hydrogen on various metals, and arranged the latter in the sequence — platinum, palladium, tungsten, iron, etc. — according to their activity. A comparison of this sequence with that obtained from experiments on the effect of the rods on the lower limit of ignition of hydrogen-rich mixtures with oxygen provides information on the identity of the recombining species.

TABLE 1.

Material of rod	Diameter of rod, cm	Temp., °C	Lower limit, mmHg, in vessel	
			without rod	with rod
Stainless steel	0.1	440	0.94	7.0
Gold	0.05	440	0.94	8.2
Tungsten	0.145	540	0.32	4.0
	0.1	440	0.53	10.3
Graphite	0.1	490	0.53	10.3
	0.1	530	0.42	7.8
	0.1	558	0.30	6.5
Quartz	0.1	440	0.94	2.34
Quartz washed with HF soln.	0.1	440	0.94	1.48

An interesting phenomenon which clearly demonstrates the branched chain character of the combustion of hydrogen is that, if a hydrogen–oxygen mixture is transferred to a reaction vessel in which a graphite or other rod has previously been placed, ignition may be observed provided that the pressure of the mixture is higher than that of the lower limit p_1 in the presence of the rod. At pressures $p < p_1$ ignition does not occur: the mixture ignites only when the rod is withdrawn from the vessel. A rod placed in a reaction vessel may be likened to a powerful pump, which extracts all the hydrogen atoms from the reaction zone. On removal of the rod, the concentration of atomic hydrogen increases very rapidly, and the mixture ignites. By placing in the reaction vessel a series of rods of varying efficiency in bringing about the recombination of hydrogen atoms, it was possible to ignite the same mixture several

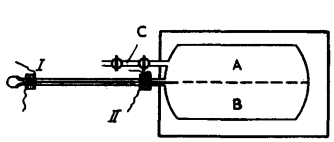

Fig. 1. Diagram of apparatus for studying the effect of rods on the lower ignition limit:
A) reaction vessel; B) subsidiary vessel;
C) electric furnace; I) and II) positions of rod.

TABLE 2. Recombination coefficients of atomic hydrogen on various surfaces.

Material of rod	T, °C	ϵ_H
$ZnOCr_2O_3$	490	1.0
Graphite	490	1.0
Gold	440	$9.8 \cdot 10^{-2}$
Platinum	388	$8.9 \cdot 10^{-2}$
Tungsten	540	$5.7 \cdot 10^{-2}$
Stainless steel	440	$2.8 \cdot 10^{-2}$
Quartz	440	$5 \cdot 10^{-4}$
Quartz washed with HF soln.	440	$3 \cdot 10^{-4}$
Pyrex washed with $K_2B_4O_7$ soln.	440	$1.9 \cdot 10^{-5}$

times by successively withdrawing rods from the reaction zone. The method described here of controlling the ignition of gaseous mixtures by means of rods strongly recalls the control of the radioactive disintegration of uranium nuclei by means of cadmium rods or boron steel rods, which strongly absorb fission neutrons. This analogy does not appear fortuitous when it is remembered that the above reaction of the combustion of hydrogen and the nuclear disintegration of uranium are both branched chain processes.

II. STUDY OF THE KINETICS AND MECHANISM OF THE COMBUSTION OF HYDROGEN AND CARBON MONOXIDE BY THE e.s.r. METHOD

1. Kinetics and Mechanism of the Combustion of Hydrogen at Low Pressures

The possibility of identifying directly all types of active centres involved in chain propagation in the oxidation of hydrogen, and of measuring their absolute concentrations, has appeared comparatively recently, after the discovery of the phenomenon of electron spin resonance (e.s.r.)[38] and construction of the appropriate instruments[39]. A great advantage of the e.s.r. method is that it permits the detection, without disturbance to the course of the reaction, not only of atoms but also of many radicals. The method was first used in the study of gas-phase chemical reactions, by Panfilov et al.[40] in the Institute of Chemical Physics of the USSR Academy of Sciences in 1960. They examined a low-pressure flame in hydrogen–oxygen mixtures with the aim of detecting atomic hydrogen and measuring its concentration. For this purpose they used the flow technique illustrated diagrammatically in Fig. 2. The low-pressure flame was established in a quartz tube *1* heated by the electric furnace *3*, placed directly above the EPR-12 cavity *2*. At pressures slightly exceeding that of the lower limit these workers found, in full agreement with Semenov's conclusions, immense concentrations of atomic hydrogen, which under certain conditions reached 10–15% of the initial hydrogen. Subsequently Panfilov[41] made a detailed study of the kinetics of the combustion of hydrogen as a function of the composition of the mixture. By measuring directly the concentration of hydrogen atoms and the variation in the concentration of molecular oxygen during the reaction, he showed that the rules deduced by Semenov, neglecting the wall destruction of oxygen atoms and hydroxy-radicals on the surface of the reaction vessel in hydrogen-rich mixtures, were completely satisfied.

The technique of using e.s.r. to study gas reactions has recently been considerably improved. It has become possible[42,43] to investigate low-pressure flames directly inside the e.s.r. cavity. Platinum wires (d = 0.2 mm) arranged along the walls of the reaction vessel and enclosed in a quartz sheath have been used to heat the reaction mixture. Such a reaction vessel, when placed inside an e.s.r. cavity, has hardly any effect on the Q factor of the latter, although the sensitivity of the instrument is slightly diminished. Tubes of larger diameter have come to be used[44], which enables flames to be obtained at lower pressures.

Using a reaction vessel heated with platinum filaments[43] and placed in an e.s.r. cavity, Balakhnin et al.[45] were in 1964 the first to observe the e.s.r. spectrum of oxygen atoms in a low-pressure hydrogen–oxygen flame (at 580° and 6 mmHg). The concentration of atomic oxygen proved to be very high. It depended greatly on the composition of the mixture. In a mixture containing ~ 15% of hydrogen and 85% of oxygen, atomic oxygen represents about 5% of the total pressure or 0.3 mmHg. The investigations showed that the concentration of oxygen atoms, while being greatest in oxygen-rich mixtures, fell as hydrogen was added. In an equimolecular mixture the concentrations of oxygen and hydrogen atoms are comparable, and in hydrogen-rich mixtures the concentration of hydrogen atoms far exceeds that of oxygen atoms. The first qualitative result obtained is fully consistent with conclusions drawn from an examination of the ratio of the kinetic constants described in the Introduction to the present Review.

In the same year 1964 Balakhnin et al.[46], employing a quartz reaction vessel with an absorbing cell completely filling the cavity, observed higher concentrations of hydroxy-radicals in low-pressure hydrogen–oxygen flames. Work with a new design of absorbing cell has shown[47-50] that the microwave absorption spectrum of hydroxy-radicals is due to electric dipole transitions, the intensity of which exceeds by several orders of magnitude that of the usual e.s.r. lines caused by magnetic dipole transitions. The concentration [configuration (?) (Ed. of Translation)] of the absorbing cell used enabled not only hydroxy-radicals but also hydrogen and oxygen atoms to be detected, since it covers antinodes both of magnetic and of electric components of the ultrahigh-frequency (UHF) field.

Fig. 3 gives the e.s.r. spectra of H and O atoms and OH and OD radicals recorded in low-pressure hydrogen–oxygen and deuterium–oxygen flames.

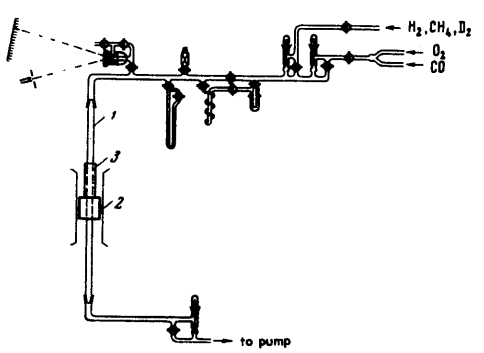

Fig. 2. Diagram of flow apparatus for the e.s.r. study of low-pressure flames.

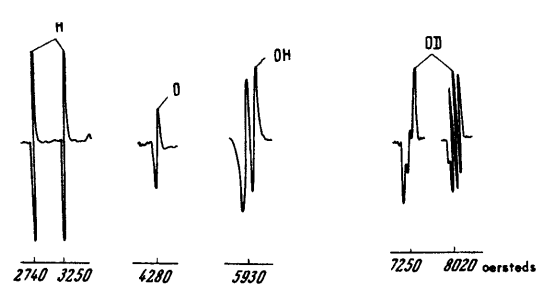

Fig. 3. Electron spin resonance spectra of H and O atoms and of OH and OD radicals obtained in low-pressure H_2–O_2 and D_2–O_2 flames.

The first stage has recently been completed[51] of investigations on the measurement of the absolute concentrations of hydrogen and oxygen atoms and hydroxy-radicals in low-pressure hydrogen–oxygen flames as functions of the composition of the mixture. In Fig. 4 the concentrations of hydrogen and oxygen atoms are plotted on the same scale, while for hydroxy-radicals the scale has been increased hundredfold. Fig. 4 also shows the variation in the quantity of water formed. The first striking feature is the parallelism between the curves for the variation in the concentration of hydroxyl and water, which pass through a maximum in the vicinity of the equimolecular composition. As noted in the Introduction, proportionality between the total concentration of hydroxyl and the quantity of water formed was at one time established by Avramenko. Such a relation arises directly from the mechanism of the oxidation of hydrogen, according to which the reaction velocity is given by the formula $w = k_1[OH][H_2]$. As was to be expected, the contribution of reaction (7), the destruction of hydroxyl on the walls, is negligible.

Fig. 4 shows that the concentration of atomic oxygen is a maximum for a mixture containing about 20% of hydrogen and 80% of oxygen. As the reactant gas is enriched with hydrogen, the concentration of oxygen atoms drops sharply. In a mixture containing 80% of hydrogen and 20% of oxygen, the concentration of oxygen atoms is $\sim 10^{14}$ cm^{-3}, while that of atomic hydrogen in this mixture is a maximum, amounting to approximately 1.3×10^{16} cm^{-3}, which exceeds the concentration of oxygen atoms by a factor of > 100. On replacement of part of the hydrogen by oxygen, the concentration of hydrogen atoms falls linearly. At the point corresponding to 20% H_2 + 80% O_2 the concentration of oxygen atoms exceeds that of hydrogen atoms by more than 50%. In an equimolecular mixture the concentration of hydrogen atoms exceeds that of oxygen atoms by a factor of about 10. However, in view of the fact that the rate constant for the destruction of oxygen atoms exceeds the corresponding constant for hydrogen atoms by a factor of about 5,[52] the heterogeneous recombination of oxygen atoms cannot be neglected. The greater rate of loss of oxygen atoms in comparison with hydrogen atoms is confirmed by curves *2* and *1* for the variation in their concentrations

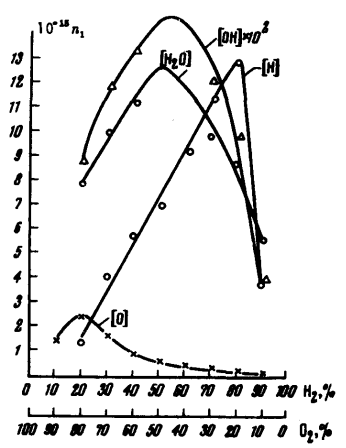

Fig. 4. Dependence of concentrations of H and O atoms and of OH radicals, and of the quantity of water formed, on the composition of the H_2–O_2 mixture.

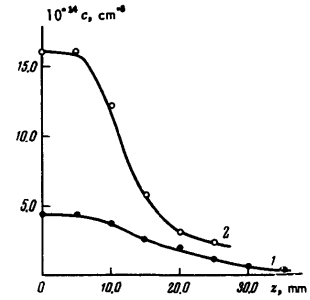

Fig. 5. Fall in concentration of atoms with distance between furnace and resonator: 1) H; 2) O.

with distance (Fig. 5), obtained by e.s.r. measurements[53] on the combustion products extractable from the reaction zone at a high linear velocity.

If the absolute concentrations of all the active centres in the combustion zone can be calculated[54–56], with simultaneous measurement of the quantity of water formed and of oxygen consumed, it will be possible to attempt to estimate the rate constants for the elementary reactions (1)–(3).

According to the above scheme for the burning of hydrogen, the reaction velocity is

$$\frac{d[H_2O]}{dt} = k_1[OH][H_2].$$

It is assumed that the contribution of reaction (7), loss of hydroxy-radicals on the walls, which also results ultimately in the formation of water, is small. By means of this equation, with the dependence of $[H_2O]$, $[OH]$, and $[H_2]$ on time of contact known, it is not difficult to calculate k_1. Such determinations have been made for an equimolecular mixture at p = 2.86 mmHg and four temperatures (900°, 943°, 993°, and 1052°K). The following expression was obtained for k_1

$$k_1 = (2 \pm 0.8) \times 10^{-10} e^{-\left(\frac{86\,100 \pm 1200}{RT}\right)} \text{ cm}^3 \text{ s}^{-1} \text{ mol.}^{-1},$$

which can be regarded as showing good agreement, within the limits of experimental error, with the value measured by Avramenko and Lorentso[57].

The rate constant k_2 of reaction (2) was calculated by means of the equation

$$\frac{d(O_2)}{dt} = -k_2[H][O_2].$$

Measurements were made, under the conditions described above, of the quantity of oxygen consumed and of the absolute concentrations of hydrogen atoms as functions of the time of contact. The value obtained for k_2 was

$$k_2 = (1.7 \pm 0.7) \times 10^{-10} e^{-\left(\frac{16\,600 \pm 1200}{RT}\right)} \text{ cm}^3 \text{ s}^{-1} \text{ mol.}^{-1},$$

which agrees well with many earlier determinations[22,58–63].

We have seen above that in hydrogen-rich mixtures with oxygen, $[H] \gg [O] \gg [OH]$. In this case the loss of oxygen atoms and hydroxy-radicals on the walls can be neglected, and hence it can be assumed that

$$\frac{d[O]}{dt} = \frac{d[OH]}{dt} = 0.$$

From the scheme for the combustion of hydrogen we have

$$\frac{d[O]}{dt} = k_2[H][O_2] - k_3[O][H_2] = 0, \quad (1)$$

$$\frac{d[OH]}{dt} = -k_1[OH][H_2] + k_2[H][O_2] + k_3[O][H_2] = 0. \quad (2)$$

Subtracting Eqn.(2) from (1), we obtain

$$\frac{[O]}{[OH]} = \frac{k_1}{2k_3}. \quad (3)$$

Measurements of this concentration ratio for hydrogen-rich mixtures showed that at 993°K and 2.55 mmHg its value was [O]/[OH] = 3. At this temperature $k_1 = 2.4 \times 10^{-12}$ cm^3 s^{-1}.

Eqn. (3) yielded for k_3 the value

$$k_3 = (0.3 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1},$$

which is also close to that found previously by other workers [22,64].

2. Kinetics and Mechanism of the Combustion of Carbon Monoxide in the Presence of Small Additions of Hydrogen

Another system which obeys the laws of branched chain reactions is the combustion of carbon monoxide in the presence of small additions of hydrogen, water vapour, or any other substance which can act as hydrogen-donor. It is assumed [22,66,67] that the combustion of carbon monoxide in the presence of hydrogen at low pressures takes place in conformity with the above scheme for the combustion of hydrogen, except that reaction (1) is replaced by the reaction

$$OH + CO \rightarrow CO_2 + H, \quad (8)$$

in which the same chain carriers — hydrogen and oxygen atoms and hydroxy-radicals — are assumed as before. The rate constants of almost all the elementary reactions are known.

It is readily seen that, when the added hydrogen constitutes a few or a fraction of one per cent of the whole mixture, reaction (3), together with the chain-branching reaction (2), becomes rate-determining. Under these conditions the rates of reactions (2) and (3) are comparable. Similar considerations [22] show that, with low H_2 contents in the mixture, reaction (5) — the loss of oxygen atoms on the surface of the reaction vessel — begins to compete with reaction (3). Hence follows the necessity for taking into account reaction (5) together with the loss of hydrogen atoms. The contribution of reaction (7) is very small in comparison with that of reaction (8), which occurs at a very high rate (high rate constant [57]

$$k_8 = 4.8 \times 10^{-13} \sqrt{T}\, e^{-\frac{5700}{RT}} \text{ cm}^3 \text{ s}^{-1},$$

and high concentration of carbon monoxide).

It is to be expected from the above that the concentration of hydrogen and oxygen atoms would be comparable, and that of hydroxy-radicals considerably lower. With the appearance of the e.s.r. method it became possible to test quantitatively the scheme for the combustion of carbon monoxide. Investigations were first made of low-pressure carbon monoxide–oxygen flames containing various quantities of hydrogen. A flow-type apparatus was used with a quartz reaction vessel heated by an electric furnace. Active particles were sought among the reaction products about 10 mm below the end of the electric furnace. A stoichiometric mixture of carbon monoxide and oxygen was studied, with variation in the amount of hydrogen added, in the temperature of the vessel from 580° to 700°, and in the pressure of the reacting gases from 2 to 10 mm. Hydrogen atoms were first detected in a $2CO + O_2 + xH_2$ mixture by Azatyan et al. [68] in 1961. Measurements made by these workers showed that, when the partial pressure of hydrogen is varied from 0.06 to 0.39 mmHg, with a total pressure of the reactant gas of 4.3 mmHg, the partial pressure of hydrogen atoms varies from 0.04 to 0.1 mmHg, which constitutes some 10% of the initial hydrogen concentration.

In the same year 1961 Azatyan et al. [69] observed high concentrations of atomic oxygen with the reaction vessel at 607–650° and 5.5 mmHg, and measured the concentration of atomic hydrogen under the same conditions. At low hydrogen contents the concentration of atomic oxygen exceeded that of atomic hydrogen. With increase in the hydrogen content, the concentration of oxygen atoms rapidly reached a maximum and then fell sharply, while the concentration of atomic hydrogen steadily increased, becoming several times greater than that of oxygen atoms. In some cases the sum of the partial pressures of hydrogen and oxygen atoms reached 2% of the total pressure.

Quite recently, in 1965, Gershenzon et al. [70], using a reaction tube with an expanded portion which completely fills the e.s.r. cavity, have observed large concentrations of hydroxy-radicals among the products of the combustion of carbon monoxide in the presence of hydrogen.

The distribution curves for all active species measured in this work are reproduced in Fig. 6, from which it is seen that the concentration of hydroxy-radicals is much lower than those of hydrogen and oxygen atoms, which are comparable. At low contents of molecular hydrogen the concentration of oxygen atoms exceeds that of hydrogen atoms. Thus all types of active centres responsible for the development of a branched chain reaction have been detected in the carbon monoxide–oxygen system containing small additions of molecular hydrogen, and their absolute quantities have been measured. The concentrations of these species were in qualitative agreement with estimated values obtained on the basis of the known rate constants for the elementary reactions (8), (2), and (3).

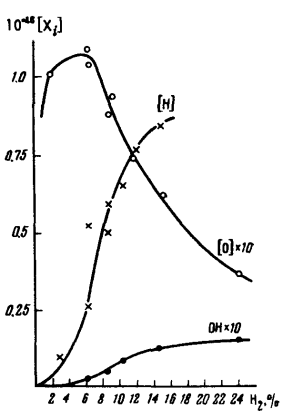

Fig. 6. Variation in concentration of H and O atoms and of OH radicals in $2CO + O_2$ mixture with percentage content of hydrogen.

On the basis of the values obtained for almost all the rate constants of the elementary reactions constituting the mechanism of the combustion of hydrogen at pressures close to the lower ignition limit, the first attempt was made to describe the kinetics of the combustion of these mixtures in the spontaneous ignition peninsula. For this purpose the following system of kinetic equations was set up to describe the time variation in all the starting materials and intermediate products

$$\frac{\partial [H]}{\partial t} = k_1[OH][CO] - k_2[H][O_2] + k_3[O][H_2] + D_H\Delta^2[H];$$

$$\frac{\partial [O]}{\partial t} = k_2[H][O_2] - k_3[O][H_2] + D_O\Delta^2[O];$$

$$\frac{\partial [OH]}{\partial t} = 2k_2[H_2][O_2] - k_1[OH][CO] + k_2[H][O_2] + k_3[O][H_2] + D_{OH}\Delta^2[OH];$$

$$\frac{\partial [CO]}{\partial t} = -k[OH][CO];$$

$$\frac{\partial [O_2]}{\partial t} = -k_0[H_2][O_2] - k_2[H][O_2];$$

$$\frac{\partial [H_2]}{\partial t} = -k_0[H_2][O_2] - k_3[O][H_2],$$

at $t = 0$, we have $[H] = [O] = [OH] = 0$. The boundary conditions are[33] $n_w \pm S(du/dx)_w = 0$, where n_w is the concentration of active centres near the wall and $S = 4\lambda/3\epsilon$, λ being the mean free path and ϵ the coefficient of destruction of active particles.

This set of differential equations cannot be solved analytically. It has been studied on an EVM-20 electronic computer.

The mixture $2CO + O_2$ was examined[70] with a content of molecular hydrogen varying from 1.5% to 10% at a total pressure of 1–8 mmHg and at the three temperatures 853°, 893°, and 923°K. The diameter of the reaction tube was 10 mm.

The first three equations of the above set contain diffusion terms representing the loss of active centres on the walls. In solving the system, the question arose of the possibility of replacing it by the simpler term $k(x)$, where k is the rate constant of heterogeneous chain termination and (x) the concentration of active centres. In the diffusion-controlled range of the loss of active centres, we have[24,71] $k = 23.2D/d^2$, where D is the diffusion coefficient of the active centres and d the diameter of the reaction vessel. In the kinetically controlled region of heterogeneous chain termination, $k = \epsilon u/d$ where ϵ is the recombination coefficient of active particles on the surface of the reaction vessel and u their thermal velocity. As long ago as 1931 Bursian and Sorokin showed[72] that, when the extent of combustion of the starting materials was small, i.e. in the initial stages of the process, such substitution is permissible, provided that the reaction velocity is limited by the reaction of one type of active centre, which is destroyed at each collision with the wall.

In 1943 Semenov[33] showed that such substitution was also possible when the rate-controlling active centre recombines on the wall in the kinetically controlled range, i.e. when $k = \epsilon u/d$. In order to establish the possibility of such substitution with more than one rate-controlling active centre (in this case three) and when the burning-up of the starting materials is not neglected, the solution was undertaken of the two sets of differential equations, with diffusion terms and with $k(x)$ terms. Values for the rate constants of the elementary reactions employed in the combustion of hydrogen (Table 3) were used in the solution.

TABLE 3.

Reaction	Value of constant	Ref.
$H_2 + O_2 \rightarrow 2OH$	$10^{-12} e^{-\frac{45\,000}{RT}}$ cm³ s⁻¹	24
$OH + CO \rightarrow CO_2 + H$	$4.8\times10^{-13}\sqrt{T}\,e^{-\frac{5700}{RT}}$ cm³ s⁻¹	57
$OH + H_2 \rightarrow H_2O + H$	$7\times10^{-12}\sqrt{T}\,e^{-\frac{10\,000}{RT}}$ cm³ s⁻¹	57
$H + O_2 \rightarrow OH + O$	$1.3\times10^{-10} e^{-\frac{15\,900}{RT}}$ cm³ s⁻¹	22
$O + H_2 \rightarrow OH + H$	$1.1\times10^{-10} e^{-\frac{11\,700}{RT}}$ cm³ s⁻¹	22
walls $H \rightarrow {}^1/_2 H_2$	$13.1\sqrt{T}\,e^{-\frac{5400}{RT}}$ s⁻¹	52
walls $O \rightarrow {}^1/_2 O_2$	$60\sqrt{T}\,e^{-\frac{6100}{RT}}$ s⁻¹	52
walls $OH \rightarrow {}^1/_2 H_2O_2$	$k_7 = k_5$	

The value of k_7 at high temperat res being unknown, it was taken to be equal to k_5.

Fig. 7 illustrates the solutions as the variation of the concentrations of active species with time. The points represent the solution of the simplified system. Agreement is seen to be good throughout the curves. Consequently replacement of the diffusion terms by $-k(x)$ is permissible in this case, too. In conformity with the branched chain character of the reaction, the curves representing the growth in active particles with time show an induction period, which becomes shorter with rise in temperature and in pressure. The concentration of active centres rapidly reaches a maximum, and then falls slowly. At points corresponding to maximum populations of the active centres, the concentrations of hydrogen and oxygen atoms are comparable, while the concentration of hydroxy--radicals is considerably lower. At small hydrogen concentrations the concentration of oxygen atoms exceeds that of hydrogen atoms. All these results agree well with experimental data, which is evidence of the correctness of the rate constants used for the individual elementary reactions in solving the set of equations.

An attempt was made to vary the rate constants — k_4, k_5, and k_7 — for the loss of active centres. When operating in the kinetically controlled range of heterogeneous chain termination, the surface of the reaction vessel was

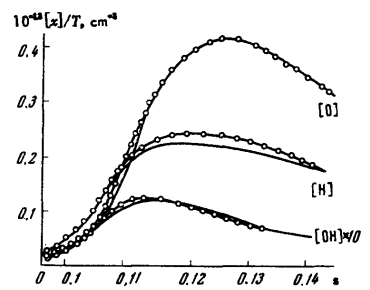

Fig. 7. Kinetics of the formation of active species in the $2CO + O_2 + 1.5\% H_2$ flame (theoretical curves).

quite often changed from one experiment to another, which directly affected the recombination constants. Analysis showed that the magnitude of the constant k_5, for the loss of oxygen atoms on the walls, had the greatest effect, with small additions of hydrogen, on the concentration of all types of active centres. The probable reason is that under these conditions the rate of reaction (3) considerably exceeds the rate of branching (2).

III. METHOD OF DETERMINING RATE CONSTANTS OF THE PRIMARY REACTIONS OF HYDROGEN AND OXYGEN ATOMS WITH VARIOUS COMPOUNDS

A good knowledge of detailed mechanisms of the combustion of hydrogen and carbon monoxide in the vicinity of their limits of spontaneous ignition enabled Azatyan et al.[22] to propose a new, improved method for determining the rate constants of the elementary reactions of hydrogen and oxygen atoms with various substances. The method is based on a remarkable property of chain processes, their high sensitivity to chemically active impurities. It is well known that minute additions of such substances are able to change sharply the reaction velocity, increasing or decreasing it several hundredfold or thousandfold. Thus, for example, small additions of iodine vapour to a mixture of hydrogen and oxygen can markedly diminish the rate of burning of hydrogen and considerably narrow the range of spontaneous ignition[73]. Fig. 8 gives the upper limit of ignition for a hydrogen–oxygen mixture (curve *1*) as a function of temperature. Curves *2* and *3* have been obtained for the same mixture but containing 0.004% and 0.006% of iodine. The lowering of the limit is obviously associated with the bulk removal of hydrogen atoms: $H + I_2 \rightarrow HI + I$. The iodine atom is known to be considerably less active than the hydrogen atom, and is unable to continue the hydrogen-oxidation chain.

Small additions of hydrocarbons, aldehydes, alcohols, acids, and many other substances have similar effects to iodine on the rate of burning of hydrogen. The action of various quantities of ethane on the lower limit of spontaneous ignition of the mixture $4H_2 + O_2$ can be cited as an example of the inhibiting action of small additions of a hydrocarbon[74]. It is seen from Fig. 9 that the lower limit gradually rises with increasing content of ethane in the mixture.

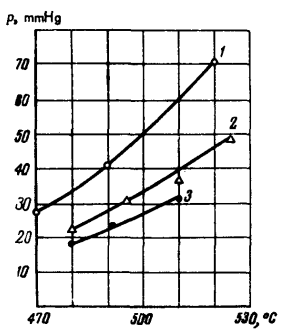

Fig. 8. Effect, on the upper ignition limit of $2H_2 + O_2$, of small additions (%) of iodine vapour:
1) 0; 2) 0.004; 3) 0.006.

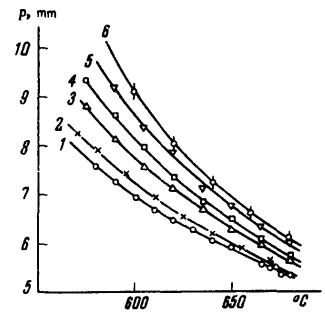

Fig. 9. Temperature dependence of lower ignition limit of $4H_2 + O_2 + xC_2H_6$ mixture for different values of x (%):
1) 0; 2) 0.0995; 3) 0.2006; 4) 0.3004; 5) 0.4070; 6) 0.4982.

Very clear cases exist of the promotion of burning by the presence of small additions of active substances. Such an example is provided by the combustion of carbon monoxide in oxygen containing small amounts of hydrogen, which we have examined previously[22,75]. As is known, an absolutely dry mixture of carbon monoxide and oxygen does not ignite, or does so, if at all, under different pressure and temperature conditions. However, it is sufficient to add a few per cent of hydrogen or water vapour to make the mixture readily ignitable. Fig. 10 illustrates how a carbon monoxide–oxygen mixture can be more readily ignited as the concentration of hydrogen added to it increases[22,75]. It was found that not only hydrogen and water vapour but also all compounds whose molecules contain hydrogen — all hydrocarbons and many other substances — possess these properties. As example of the promoting action of small additions we may cite the dependence of the lower carbon monoxide–oxygen limit on the presence of ethane[76]. It is seen from Figs. 9 and 11 that additions of ethane inhibit burning in one system and promote it in another. This dual effect of the same substance on rate of burning was found not only for different systems but also in the

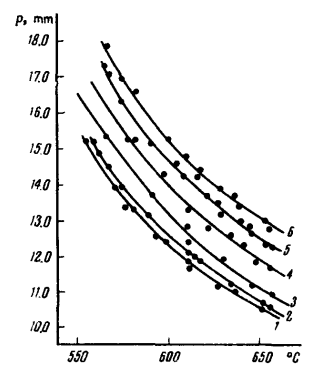

Fig. 10. Temperature dependence of lower limit of $2CO + O_2 + xH_2$ mixture for different values of x (%):
1) 3.79; 2) 3.28; 3) 2.14; 4) 1.48; 5) 1.06; 6) 0.78.

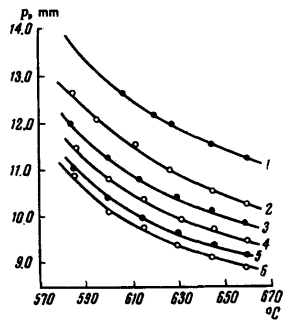

Fig. 11. Temperature dependence of lower ignition limit of $2CO + O_2 + xC_2H_6$ mixture for different values of x (%): 1) 0.0225; 2) 0.0389; 3) 0.0555; 4) 0.074; 5) 0.097; 6) 0.141.

same system[75,76]. If, for example, the concentration of ethane in the carbon monoxide–oxygen reactant mixture is further increased, a point is reached at which the limit begins to rise[76], as is well seen from Fig. 12. The dual effect of the simplest hydrocarbon, methane, on the lower carbon monoxide–oxygen limit was first reported in Ref. 77.

Let us consider in sequence the causes of the inhibiting action of small additions of active impurities on the combustion rate of hydrogen and its limits, and the dual effect of these substances on the combustion of carbon monoxide and oxygen and its lower limit of spontaneous ignition. The work of Voevodskii and Tikhomirova[78] simultaneously with that of Baldwin[59] showed that the inhibiting action of ethane and other hydrocarbons on the hydrogen–oxygen ignition limits is due to the additional homogeneous loss of hydrogen atoms by the reaction

$$H + C_2H_6 \rightarrow H_2 + C_2H_5. \quad (9)$$

followed by the reaction

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2. \quad (10)$$

The result of reactions (9) and (10) is to replace an active hydrogen atom by a relatively inactive HO_2 radical.

Investigations of low-pressure hydrogen–oxygen flames by the e.s.r. method show that the concentration of all

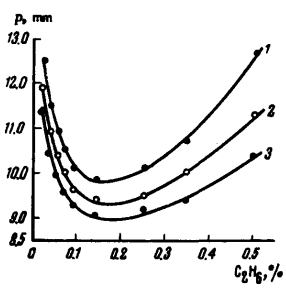

Fig. 12. Dependence of lower limit of spontaneous ignition of $2CO + O_2$ on percentage of C_2H_6 in mixtures at (°C): 1) 610; 2) 630; 3) 650.

active species — carriers of the chain oxidation of hydrogen — drops sharply on addition of the inhibitor. In this connection, the condition for the lower ignition limit in hydrogen-rich mixtures with oxygen must be written

$$2k_2[O_2][H] = k_4[H] + k_9[RH][H].$$

The left-hand side determines the rate of branching, and the right-hand side is the sum of terms determining the rates of loss of hydrogen atoms on the walls and in bulk. Hence the concentration of oxygen at the lower limit $[O_2]$ is determined by the equation

$$[O_2] = \frac{k_4}{2k_2} + \frac{k_9}{2k_2}[RH], \quad (A)$$

from which it is seen that, in full agreement with experiment, additions of an active impurity tend to raise the lower limit. When $[RH] = 0$, we have $[O_2] = k_4/2k_2$, the ratio of the rate constants for loss [of atomic hydrogen] (4) and branching (2).

The accelerating effect of small additions of various compounds RH, which act as hydrogen-donors in the combustion of carbon monoxide, can be explained by the following reactions of chain propagation and branching

$$OH + CO \rightarrow CO_2 + H, \quad (8)$$
$$H + O_2 \rightarrow OH + O, \quad (2)$$
$$O + RH \rightarrow OH + R. \quad (11)$$

Thus it is suggested that atomic oxygen, on interaction with the active additive, abstracts a hydrogen atom from the latter to form a hydroxy-radical. The flame of a carefully purified and dried mixture of carbon monoxide and oxygen has been studied by the e.s.r. method in the presence of over a score of different hydrogen-donors. The additives comprised methane, ethane, propane, butane, ethylene, propene, methanol, ammonia and several of its derivatives, and many other compounds[75,79,82]. In all cases large concentrations of hydroxy-radicals and hydrogen and oxygen atoms were detected, which increased as the impurity content increased to a certain value [RH] depending on the temperature and the nature of the additive. The inhibiting action of high concentrations [RH] is obviously due to reaction (9), which results in the bulk loss of hydrogen atoms. The e.s.r. measurements show that the concentration [RH] at which the limit begins to increase is followed by a sharp drop in the concentration of hydrogen and oxygen atoms and hydroxy-radicals[80].

The combustion of carbon monoxide in the presence of an active impurity RH can be represented by the sequence of elementary reactions (1)–(9). Mathematical analysis of the scheme by means of Semenov's method of steady-state concentrations[83] yields the following final expression for the ignition condition[76]

$$[O_2]_l^{CO} = \frac{k_4}{k_2}\left(1 + \frac{k_9[RH]}{k_4}\right)\left(1 + \frac{k_5}{k_{11}[RH]}\right), \quad (B)$$

from which it follows, in complete agreement with experiment, that the lower limit should have a high value in a mixture of carbon monoxide and oxygen ($[RH] \rightarrow 0$). With addition to it of an active impurity RH, the pressure at the lower ignition limit will fall with [RH] until reaction (9) begins to compete with reaction (2). With further increase in the impurity content beyond this concentration [RH], which can be termed a critical concentration, the lower limit begins to rise. When hydrogen is the added substance, this condition is written[22]

$$[O_2]_l^{CO} = \frac{k_4}{2k_2}\left(1 + \frac{k_5}{k_3[H_2]}\right), \quad (C)$$

where $[O_2]_1^{CO}$ is the oxygen concentration at the lower limit of the carbon monoxide–oxygen mixture containing various additions of hydrogen, and the k are the rate constants of the corresponding elementary reactions.

Unlike the method based on determination of lower limits in the kinetically controlled region of heterogeneous chain termination[84], the reaction is conducted in the diffusion-controlled region of heterogeneous destruction of active centres in the proposed method[75]. An advantage of this is the excellent reproducibility and the associated far greater accuracy of the constants obtained. Azatyan's detailed investigations[76] have shown that chain termination in the diffusion-controlled region is completely ensured by coating the walls of the reaction vessel with magnesium oxide. Let us examine the principle underlying the determination of the rate constants of reactions (9) and (3), with the combustion of hydrogen-rich mixtures with oxygen and of carbon monoxide–oxygen mixtures containing small additions of hydrogen as examples, for which purpose we consider in succession the equations to the lower limit (A) and (B), in which the heterogeneous chain-termination constants k_4 and k_5 can be calculated[75]. With cylindrical vessels

$$k = \frac{23.2\,D}{d^2} = \frac{23.2}{d^2} D_{stp} \frac{760}{(273)^{1.5}} \frac{T^{1.5}}{p} \quad \text{or} \quad k = k^0 \frac{T^{1.5}}{p}$$

where

$$k^0 = \frac{23.2}{d^2} D_{stp} \frac{760}{(273)^{1.5}}, \qquad (D)$$

D_{stp} being the diffusion coefficient of the corresponding active centre at standard temperature and pressure. Substituting for k_4 and k_5 in Eqn. (A) and replacing concentrations by pressure, we can rewrite the equation for the lower limit in a hydrogen-rich mixture with oxygen in the form

$$pp_{O_2} = \frac{k_4^0 T^{2.5}}{2k_2 \times 10^{19}} \left[1 + \frac{k_9 \times 10^{19}}{k_4^0 \times T^{2.5}} pp_{RH} \right]$$

where p is the pressure of the reactant mixture at the limit, and p_{O_2} and p_{RH} are the pressures of oxygen and the added impurity at this limit. When plotted as pp_{O_2} against pp_{RH} this is the equation to a straight line.

Fig. 13 shows the series of straight lines obtained by recalculating the lower limits as a function of temperature for the various additions of ethane shown in Fig. 9. The experimental points are seen to fit well on straight lines for the different temperatures. These straight lines make intercepts $a = k_4^0 T^{2.5}/2 \times 10^{19} k_2$ on the ordinate axis, and have a slope of $\tan\alpha = k_9/2k_2$. Dividing the latter by the former and taking logarithms, we obtain

$$\log \frac{\tan\alpha \cdot T^{2.5}}{a} = \log \frac{k_9^0 \cdot 10^{19}}{k_4^0} - \frac{E_9}{4.57} \times \frac{1}{T}$$

which represents a linear variation of $\log [T^{2.5}(\tan\alpha)/a]$ with $1/T$. Results calculated from the data in Fig. 13 are plotted in Fig. 14. In this case, too, the points lie on a straight line. From the slope of the straight line we can readily determine E_9, the activation energy of reaction (9), and from the intercept we can find k_9^0.

In this way rate constants have been determined for many elementary reactions of atomic hydrogen with molecules of various active impurities added to a hydrogen–oxygen mixture. A test of the method is provided by the boundary condition (A): at [RH] = 0 the intercepts a (Table 4) made by the straight lines on the ordinate axis at

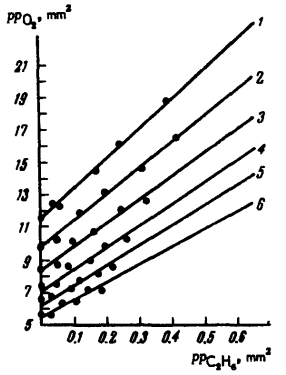

Fig. 13. Dependence of pp_{O_2} on $pp_{C_2H_6}$ at (°C):
1) 580; 2) 600; 3) 620; 4) 640; 5) 660; 6) 680.

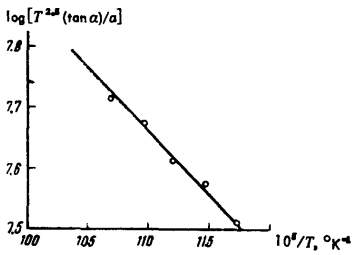

Fig. 14.

TABLE 4.

T, °C	a, mm³	$p^{H_2}p^{H_2}_{O_2}$, mm³
580	11.6	11.6
600	9.8	9.70
620	8.3	8.4
640	7.10	7.40
660	6.20	6.5
680	5.50	5.60

different temperatures should be identical with the product $p^{H_2}p^{H_2}_{O_2}$. The scatter of the values given as example in Table 4 is seen to be small.

The method can also be tested by the value of the branching rate constant k_2, which can be determined from the relationship $a = k_4^0 T^{2.5}/2 \times 10^{19} k_2$ and compared with the published value. This relationship can be rewritten in the form

$$\log \frac{a}{T^{2.5}} = \log \frac{k_4^0}{2k_2^0 \cdot 10^{19}} + \frac{E_2}{4.57} \times \frac{1}{T}.$$

The variation required by the equation is shown in Fig. 15, values of a having been taken from Table 4. The slope of the resulting straight line was used to calculate E_2, and the intercept on the ordinate axis gave k_2^0. The overall formula obtained for the constant was

$$k_2 = 2.1 \times 10^{-10} e^{-\frac{16\,600}{RT}} \text{ cm}^3\,\text{s}^{-1}\,\text{mol.}^{-1},$$

in good agreement with the corresponding published value.

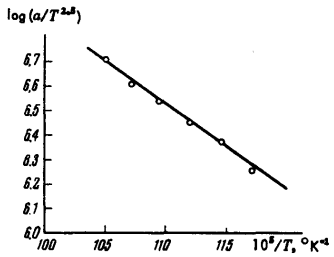

Fig. 15.

Let us now consider the method of determining the rate constant of reaction (3), for which purpose we use Eqn. (C) for the lower limit of ignition of a carbon monoxide–oxygen mixture in the presence of hydrogen. Substituting for k_4 and k_5, and replacing the concentrations $[O_2]^{CO}$ and $[H_2]$ by pressures, we can write the equation in the form

$$pp_{O_2} = \frac{(k_4^0)^{CO} \cdot T^{2.5}}{2k_2 \cdot 10^{19}} \left[1 + \frac{(k_5^0)^{CO} \cdot T^{2.5}}{k_3 \cdot 10^{19} \cdot pp_{H_2}} \right],$$

where p is the pressure at the lower limit of $2CO + O_2 + xH_2$, and p_{O_2} and p_{H_2} are the partial pressures of oxygen and hydrogen at this limit. The superscript CO attached to k_4^0 and k_5^0 indicates that these parameters relate to the above mixture. When plotted as pp_{O_2} against $1/pp_{H_2}$, this equation represents a straight line.

Fig. 16 shows the results of analysing the experimental data plotted in Fig. 10, and gives the temperature dependence of the lower ignition limit with various contents of hydrogen in the $2CO + O_2$ reactant mixture. The experimental data are seen to fit the corresponding curves well in Fig. 16. These curves make intercepts $b = k_4^0 T^{2.5}/2 \times 10^{19} k_2$ on the ordinate axis, and the slope of the straight lines is

$$\tan\alpha = \frac{(k_4^0)^{CO} \cdot T^{2.5}}{2k_2 \cdot 10^{19}} \times \frac{(k_5)^{CO} \cdot T^{2.5}}{k_3 \cdot 10^{19}}.$$

The logarithm of their ratio is

$$\log \frac{\tan\alpha}{b \cdot T^{2.5}} = \log \frac{(k_5^0)^{CO}}{10^{19} \cdot k_3^0} + \frac{E_3}{4.57} \cdot \frac{1}{T},$$

where E_3 is the activation energy of reaction (3), and k_3^0 is the preexponential factor.

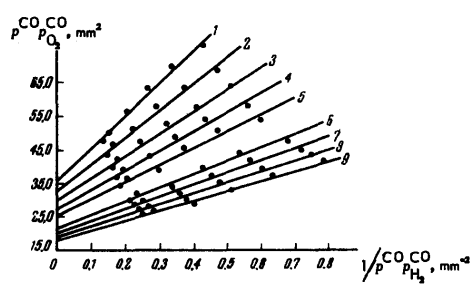

Fig. 16. Dependence of pp_{O_2} on $1/pp_{H_2}$ at (°C): 1) 570; 2) 580; 3) 590; 4) 600; 5) 610; 6) 630; 7) 640; 8) 650; 9) 660.

Fig. 17 shows that the dependence of $\log[(\tan\alpha)/bT^{2.5}]$ on $1/T$ calculated from the data plotted in Fig. 16 fit well on a straight line in this case, too. The slope of the line gave E_3, and the intercept on the vertical axis k_3^0. The expression obtained for the rate constant of the reaction was

$$k_3 = 1.1 \times 10^{-10} e^{-\frac{11\,700}{RT}} \text{ cm}^3 \text{ s}^{-1} \text{ mol.}^{-1}.$$

The value obtained[22] of E_3 = 11.7 kcal mole^{-1} considerably exceeds that calculated from the experiments of Harteck and Kopsch, and is somewhat higher than that given in Ref. 64. As has been shown above, the best agreement with experiment is obtained in fact with this value of E_3.

Let us consider the significance of the intercepts b made by the straight lines on the ordinate axis (Fig. 16) in the case of carbon monoxide–oxygen mixtures containing small additions of hydrogen. Writing Eqn. (D) for carbon monoxide–oxygen mixtures containing small additions of hydrogen and also for hydrogen–oxygen mixtures, and dividing the former by the latter, we obtain

$$(k_4^0)^{CO} = (k_4^0)^{H_2} \frac{(D_{stp})^{CO}}{(D_{stp})^{H_2}},$$

where $(D_{stp})^{CO}$ and $(D_{stp})^{H_2}$ are the respective diffusion coefficients of hydrogen atoms in the two mixtures under normal conditions. Substituting $(k_4^0)^{CO}$ in the formula for b, we have

$$b = \frac{(k_4^0)^{H_2} \cdot T^{2.5}}{2k_2 \cdot 10^{19}} \cdot \frac{(D_{stp})^{CO}}{(D_{stp})^{H_2}},$$

or, since

$$\frac{(k_4^0)^{H_2} \cdot T^{2.5}}{2k_2 \cdot 10^{19}} = p^{H_2} \cdot p_{O_2}^{H_2},$$

$$b = p^{H_2} \cdot p_{O_2}^{H_2} \cdot \frac{(D_{stp})^{CO}}{(D_{stp})^{H_2}}.$$

This means that the straight lines should make intercepts on the vertical axis[75] which are numerically equal to the product $p^{H_2} p_{O_2}^{H_2}$ at the lower limit of the hydrogen–oxygen mixture multiplied by the ratio of the diffusion coefficients of hydrogen atoms in the $CO + O_2 + xH_2$ and $H_2 + O_2$ mixtures. (When considering the lower limits of hydrogen–oxygen mixtures in the presence of RH, it was obviously necessary to take into account the appropriate correction D^{RH}/D^{H_2}. Since, however, the diffusion coefficients of hydrogen atoms in a hydrogen–oxygen mixture are very little changed by the addition of up to 1% of RH, this ratio can be taken as unity.) Azatyan's calculations showed[75] that $D^{CO}/D^{H_2} \simeq 0.72$. Comparison of the lengths of the intercepts b with the corresponding product obtained from

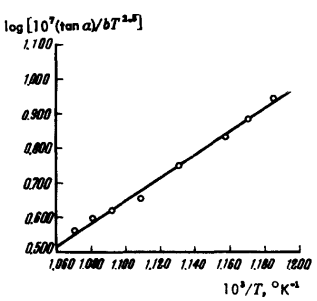

Fig. 17.

TABLE 5.

Reaction	k_0, cm³ s⁻¹ mol.⁻¹	E, kcal mole⁻¹	Ref.
$H + O_2 = OH + O$	$1.3 \cdot 10^{-10}$	15.9 ± 0.8	22
$H + CH_4 = H_2 + CH_3$	$2.0 \cdot 10^{-11}$	10.6 ± 1.0	75
$H + C_2H_6 = H_2 + C_2H_5$	$1.0 \cdot 10^{-10}$	9.5 ± 1.0	74
$H + C_2H_4 = H_2 + C_2H_3$	$1.5 \cdot 10^{-11}$	7.2 ± 1.0	86
$H + C_3H_8 = H_2 + C_3H_7$	$T=640°$	$k=4.8 \cdot 10^{-12}$	87
$H + NH_3 = H_2 + NH_2$	$0.68 \cdot 10^{-10}$	13.7 ± 0.6	88
$H + C_2H_5OH = H + C_2H_4OH$	$2 \cdot 10^{-11}$	8.1 ± 0.6	89
$H + n\text{-}C_3H_7OH = H_2 + C_3H_6OH$	$4.1 \cdot 10^{-11}$	6.4 ± 0.6	88
$H + n\text{-}C_4H_9OH = H_2 + C_4H_8OH$	$3.3 \cdot 10^{-11}$	5.1 ± 0.6	88
$O + H_2 = OH + H$	$1.1 \cdot 10^{-10}$	11.7 ± 0.7	22
$O + CH_4 = OH + CH_3$	$0.94 \cdot 10^{-10}$	8.7 ± 0.8	75,85
$O + NH_3 = OH + NH_2$	$0.32 \cdot 10^{-10}$	10.0 ± 0.5	88
$O + C_2H_4 = OH + C_2H_3$	$2.3 \cdot 10^{-10}$	8.1 ± 0.5	86
$O + C_2H_6 = OH + C_2H_5$	$1.4 \cdot 10^{-10}$	7.5 ± 1.0	86
$O + C_3H_8 = OH + C_3H_7$	$1.8 \cdot 10^{-10}$	6.2 ± 1.0	90
$O + C_4H_{10} = OH + C_4H_9$	$T=630°$	$k=1.2 \cdot 10^{-11}$	90

direct measurements of the lower limit of spontaneous ignition of hydrogen–oxygen mixtures, with the correction D^{CO}/D^{H_2} taken into account, showed good agreement between experiment and calculation. The temperature dependence of b was used to calculate the rate constant of reaction (2) as

$$k_2 = 1.3 \times 10^{-10} e^{-\frac{15\,900}{RT}} \text{ cm}^3 \text{ s}^{-1} \text{ mol.}^{-1}.$$

Eqn. (B) must be used[85] to determine the rate constants of elementary reactions of the type (11). This equation contains, besides the unknown constant k_{11}, the rate constant k_9 of the reaction $H + RH \rightarrow H_2 + R$, which is found from experimental results on the dependence of the lower limit of hydrogen-rich mixtures with oxygen containing RH as impurity. In several cases the radical R, formed in reactions (9) and (11), may interact with oxygen to form a new active centre in the main oxidation chain:

$$R + O_2 \rightarrow R'CHO + OH. \qquad (12)$$

As a result, the condition for the lower limit will contain, together with the required constant k_{11}, the additional unknown factor $k_9/(k_9 + k_{10})$.

A method which has been suggested[75] for eliminating this factor is to consider simultaneously the conditions of the lower ignition limits for the mixtures $H_2 + O_2 + xRH$ and $CO + O_2 + xRH$ deduced with reaction (12) taken into account. Table 5 gives values for the rate constants of elementary reactions of hydrogen and oxygen atoms with the molecules of several compounds, determined from the displacement of the lower limits of hydrogen–oxygen and carbon monoxide–oxygen mixtures in the presence of small additions of these compounds.

IV. USE OF e.s.r. METHOD TO ESTABLISH THE SITE AT WHICH ATOMIC OXYGEN ATTACKS A COMPLEX MOLECULE

The e.s.r. method, applied to low-pressure flames, enables us to establish the point at which a complex molecule is attacked by atomic oxygen, as has been shown in the case of the methanol molecule[81]. A low-pressure carbon monoxide–oxygen flame has been studied in the presence of small additions of methanol. It was first shown that small additions of the latter, as of other hydrogen-donors, depress the lower ignition limit. Fig. 18 illustrates the dependence of the lower limit on the methanol content for two temperatures. The low-pressure flames in $2CO + O_2 + xCH_3OH$ mixtures were investigated in an apparatus of the type illustrated in Fig. 2. Previously dried and

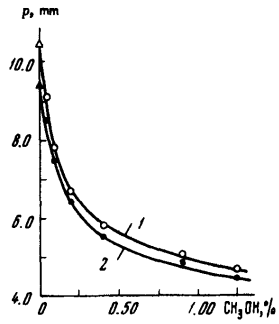

Fig. 18. Dependence of lower limit of spontaneous ignition of $2CO + O_2$ mixture on percentage content of methanol at (°C): 1) 670; 2) 690.

purified carbon monoxide was bubbled through methanol at 6°C, after which it was passed through a coil immersed in a thermostat at 0°C. The carbon monoxide saturated with the methanol vapour at 0°C was mixed through a regulating valve with a stream of carbon monoxide and oxygen, which had also first been purified and dried. The percentage of the alcohol in the stream was varied by changing the flow of carbon monoxide bubbled through it. Experiments were made over the temperature range 685–755°C at pressures of 3–7.4 mmHg with an initial alcohol content in the mixture of 0.86–1.7%. In all cases large quantities of hydroxy-radicals and hydrogen and oxygen atoms were observed in the flame. The presence of active species in the flame, as well as the depression of the lower limit with increasing concentration of methanol in the mixture, indicates that, as with the above promoters of the burning of carbon monoxide, the effective rate of chain branching is limited by the reaction of atomic oxygen with methanol, so that the mechanism of the combustion of carbon monoxide in the presence of methanol can be represented by the sequence of reactions

$$OH + CO \rightarrow CO_2 + H,$$
$$H + O_2 \rightarrow OH + O,$$
$$O + CH_3OH \rightarrow OH + CH_2OH \quad \text{or} \quad O + CH_3OH \rightarrow OH + CH_3O,$$
$$H \xrightarrow{\text{walls}} {}^1/_2 H_2,$$
$$O \xrightarrow{\text{walls}} {}^1/_2 O_2,$$
$$H + CH_3OH \rightarrow H_2 + CH_2OH.$$

It was stated above that hydroxy-radicals enter very rapidly into reaction (8). Hence by adding small quantities of CH_3OD or CD_3OH to the reacting mixture and determining the ratio of OH to OD, it might be possible to assess the point of attack. Since the maximum magnetic field strength in the EPR-2 apparatus does not exceed 6000 oersteds, whereas OD radicals are observed in stronger fields, the ratio [H]/[D] was measured on the assumption that they obeyed the same proportionality. Such substitution cannot influence the conclusion drawn by these authors, since two series of independent experiments were made with CH_3OD and CD_3OH. When CH_3OD was added as impurity, no lines at all due to D atoms were detected in the e.s.r. spectrum of the low-pressure flame. Yet the intensity of the lines due to hydrogen atoms exceeded the noise level by factors of 30–35. From the number of components in the spectrum of hydrogen and deuterium

atoms and the width of the lines, the ratio was found to be $[H]/[D] \geq 15$. This means that oxygen atoms attack preferentially the methyl group of the CH_3OD molecule. When CD_3OH was added, the low-pressure flame was found to contain large quantities of deuterium atoms and relatively few hydrogen atoms. The ratio was $[D]/[H] \simeq 6$. This means that oxygen atoms preferentially attack the CD_3 group on reaction with CD_3OH.

The change in the proportion of atoms which can be abstracted from the methyl group on passing from CH_3OD to CD_3OH is obviously associated with a difference in strength between the C–H and C–D bonds, and also between O–H and O–D, in methanol. If the difference in activation energy for abstraction by oxygen atoms of deuterium and hydrogen atoms from the methyl group is taken to be 1.2 kcal $mole^{-1}$,[91] the ratio of the rate of abstraction of a hydrogen atom from the methyl group to the rate of abstraction of a hydrogen atom from the hydroxy-group is 11. On a similar hypothesis concerning the abstraction of deuterium and hydrogen atoms from the hydroxy-group of the alcohol molecule CH_3OD, these workers showed that this ratio should exceed 8. It was thus established that at temperatures up to 755°C oxygen atoms attack preferentially the methyl group of the CH_3OH molecule.

V. INVESTIGATION OF SOME LOW-PRESSURE FLAMES BY THE e.s.r. METHOD

The above two systems unfortunately exhaust our fundamental knowledge of the detailed mechanisms of complicated chemical processes. During the forty years since the chain nature of the combustion of phosphorus was established, many new reactions which also obey the laws of branched chain reactions have been discovered: they give ignition limits which are sensitive to chemically active additions, to the diameter of the reaction vessel, to its surface properties, etc. Until recently, however, the active species – the carriers of chain oxidation – have not been identified in many systems. Great difficulties have arisen in this connection in constructing mechanisms for these reactions. We have seen above that optical spectroscopy has played a large part in developing the theory of chain reactions, in identifying hydroxy-radicals as one of the main chain-carriers, and in measuring their absolute concentrations. By this technique, incidentally, Emanuel'[92] discovered surprisingly large quantities of SO radicals in a slow chain reaction.

In view of the above discussion, it appears that electron spin resonance may play a still larger part in the study of the mechanisms of complex reactions. This method enables many radicals to be detected, as well as atoms. A combination of electron spin resonance, optical spectroscopy, and kinetic methods for studying chemical processes will undoubtedly permit a more rapid penetration into the detailed mechanisms of chemical reactions.

In the light of the above, the authors whose work is discussed below have decided to undertake a detailed examination of several systems which had formed subjects of earlier investigations.

1. Reaction of Sulphur Vapour with Oxygen

The reaction of sulphur vapour with oxygen was one of the first in which Semenov and Ryabinin[3] discovered lower and upper limits of spontaneous ignition. However, there is no indication in the literature of the detection of any active centres in this system. On the basis of indirect evidence, associated with the behaviour of the system on combustion, Semenov[24] suggested that oxygen atoms were formed.

Sarkisyan et al.[93] report the first results of an e.s.r. investigation of a low-pressure flame of sulphur vapour in oxygen. A novel feature of the experimental technique, compared with that discussed above, is the evaporator reaction vessel used for work both with solids and with liquids whose vapours undergo combustion. The diagram (Fig. 19) shows that the vessel consists of two coaxial tubes *1* and *2*. The outer tube has a widened portion *3* in an e.s.r. cavity resonator, which enables magnetic and electric components of the UHF field to be used. Use of the vessel illustrated in Fig. 19 became possible as a result of the improvement described in another paper[44]. The sulphur was placed in the cup *4* of the inner tube. A gentle stream of an inert gas was supplied through this tube, and entrained the sulphur vapour by flowing over the sulphur heated by means of a special furnace *5*. The gases emerged through the nozzle *6* into the combustion zone, where they mixed with oxygen supplied through the outer tube. The temperature of the combustion zone was maintained by means of the furnace *7*. The inner tube could be moved vertically by means of the ground glass joint *8*, which made it possible to move the combustion zone. The part of the reaction vessel located in the resonator was heated by a stream of hot air. By lowering the combustion zone, the flame could thus be drawn into the resonator. Experiments were made at 300–400°C, and the pressure of the mixture was varied over the range 1.5–3 mmHg.

Under these conditions large quantities of SO radicals and O atoms were observed in the flame. Three single lines were observed for the SO radical, which coincided with published e.s.r. spectral lines for SO radicals obtained by means of an electric discharge in sulphur dioxide[94,95]

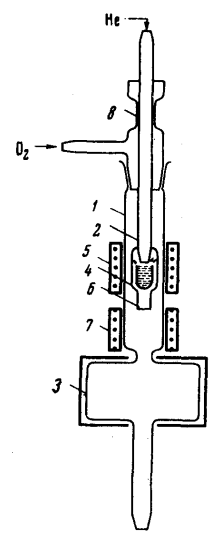

Fig. 19. Diagram of evaporator reaction vessel.

or by the reaction O + COS = CO + SO.[96] The concentration of oxygen atoms reached 25–30% of the initial oxygen, and that of SO was an order of magnitude lower. Experiments showed that small additions of methane resulted in a diminution in the concentration of oxygen atoms. At the same time lines were observed in the spectrum characteristic of the hydroxy-radical, their appearance obviously being due to the reaction $O + CH_4 \rightarrow OH + CH_3$.

In 1954 Semenov[98] considered the possible role of diradicals in chain reactions, and suggested the following mechanism for the diradical oxidation of sulphur vapour

$$S_8 = \dot{S}_7 + \dot{S},$$
$$\dot{S} + O_2 = \dot{S}O + \dot{O},$$
$$\dot{O} + S_8 = \dot{S}O + \dot{S} + S_6,$$
$$\dot{S}O + O_2 = SO_2 + \dot{O},$$
$$O + O_2 + M = O_3 + M,$$
$$SO_2 + O = SO_3,$$
$$O \xrightarrow{\text{walls}} {}^1/_2 O_2.$$

As we see, the main carriers of the diradical chain combustion of sulphur — oxygen atoms and SO radicals — have been detected. It will be shown further that sulphur atoms cannot be observed, either in this system or in other systems containing sulphur. The failure to detect sulphur atoms is obviously associated with their great reactivity, as a result of which their equilibrium concentration is considerably lower than the sensitivity of the e.s.r. instrument. Further investigation of the kinetics and the mechanism of the combustion of sulphur vapour will in the very near future enable the mechanism of this process to be finally established.

2. Investigation of Low-Pressure Carbon Disulphide–Oxygen Flames

The burning of carbon disulphide in oxygen was studied in detail by Kondrat'ev,[99] and was also investigated by Voronkov and Semenov[100]. The reaction was shown to develop by a branched chain mechanism. Using a flow technique, Kondrat'ev observed the interesting phenomenon of a sharp change in colour of the flame on passing from mixtures rich in oxygen to those poor in oxygen near the stoichiometric mixture. Analysis established the formation of COS and sulphur as intermediate products. The radical CS was detected in mixtures rich in carbon disulphide. The principal final reaction products were sulphur dioxide and carbon monoxide. Fig. 20 illustrates the yields of intermediate and final reaction products as functions of $\alpha = [O_2]/[CS_2]$. Spectroscopic investigations have shown that the concentration of CS radicals, which is very low near $\alpha \simeq 2.5$, increases rapidly as α decreases, i.e. with enrichment of the mixture with carbon disulphide.

As in previous work, the e.s.r. investigation of low-pressure carbon disulphide flames was conducted under flow conditions. The flame was produced in the part of the tube located in the e.s.r. resonator. Experiments were made over the temperature range 200–500°C and at 6 mmHg. The ratio α varied over the range 0.8–14. Azatyan et al.[101] observed large quantities of oxygen atoms in oxygen-rich mixtures, their spectrum being identified from the g factor of 1.5 and from the fine structure. The

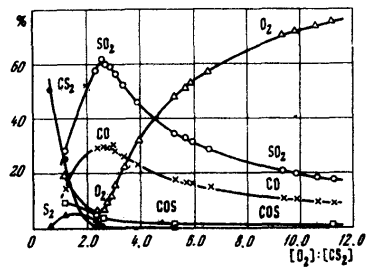

Fig. 20. Composition of combustion products of $CS_2 + O_2$ mixtures as function of $\alpha = [O_2]/[CS_2]$.

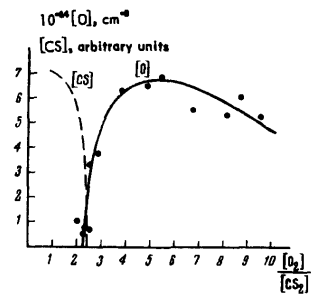

Fig. 21. Dependence of concentration of oxygen atoms on α.

assignment of the spectrum to atomic oxygen was also proved chemically: on addition of small amounts of molecular hydrogen to the reactant mixture, the concentration of oxygen atoms falls, while lines characteristic of the hydroxy-radical and hydrogen atoms appear, obviously as a result of the reaction $O + H_2 = OH + H$.

The dependence of the concentration of oxygen atoms on α is shown in Fig. 21, from which it is seen that at $\alpha \simeq 2.5$ the concentration is lower than the sensitivity of the e.s.r. instrument. Slight enrichment of the mixture with oxygen results in a sharp increase in the concentration of atomic oxygen. With further increase the concentration reaches a maximum and then slowly falls. Thus the atomic oxygen curve is, as it were, the mirror image of the curve for the variation in CS found by Kondrat'ev and included in the diagram on an arbitrary scale. This at first glance peculiar shape of the atomic oxygen curve seems to us to be due to reaction of the oxygen atoms with intermediate compounds, primarily with COS and S_2, which are the main intermediates in the region $\alpha < 2.5$. Quite recently a still further active species — the SO radical — has been detected in this system in the Institute of Chemical Physics of the USSR Academy of Sciences. Investigations will be continued on low-pressure carbon disulphide flames with the aim of elucidating the reaction mechanism.

3. Study of Low-Pressure Hydrogen Sulphide Flames

Great interest attaches to e.s.r. investigations of low-pressure hydrogen sulphide flames. It has been noted above that large quantities of SO radicals have been observed, and several of their properties studied, in the slow oxidation of hydrogen sulphide at pressures above the

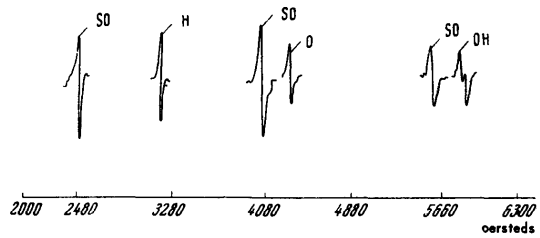

Fig. 22. Electron spin resonance spectrum of H and O atoms and OH and SO radicals detected in low-pressure hydrogen sulphide flames.

second limit of spontaneous ignition (100–200 mmHg). Emanuel'[92], and later Semenov[24], suggested mechanisms for the chain oxidation of hydrogen sulphide. The optical absorption spectra of SO, OH, and S_2 radicals had been observed[102] in the hydrogen sulphide flame before the e.s.r. method was applied. The absorption spectrum of sulphur monoxide — though in the form of the dimer S_2O_2 — has been observed[103] in the flash photolysis of hydrogen sulphide–oxygen mixtures under isothermal conditions. Mass-spectroscopic examination of the flame near the third limit indicates the existence of the S_2O radical[104]. The HS radical has not yet been detected in the flame.

Sachyan and Nalbandyan[105] have been able to observe large concentrations of hydrogen atoms and oxygen atoms in an e.s.r. study of low-pressure hydrogen sulphide flames using a heated reaction vessel placed in the e.s.r. resonator. Experiments were made at pressures up to 10 mmHg over the temperature range 350–450°C. In these experiments a signal due to atomic oxygen was detected at low hydrogen sulphide contents, but disappeared when the latter reached 25% of the whole mixture. The signal of atomic hydrogen was found at a hydrogen sulphide content of ~ 15% of the initial mixture, and became more intense as the latter increased to 45–50%.

In order to detect spectra possessing electric dipole transitions, a quartz cell completely filling the resonator was used. An electric furnace was placed above the resonator, which was heated up with hot air both to eliminate the formation of a deposit in the quartz tube and also in order to ignite the combustible mixture directly in the resonator space in the wide part of the quartz tube. Under these conditions Gershenzon et al. [106] observed the signals of hydroxy-radicals in the form of an unresolved doublet, and also three single signals in different parts of the magnetic field, due to the SO radical. Fig. 22 shows the spectra of the hydrogen and oxygen atoms and the OH and SO radicals obtained. It was expected that HS radicals would also be present in the flame, but all searches, in different systems and under different conditions, were fruitless. This is, perhaps, due to rapid reaction of HS radicals with oxygen.

We see that, among the systems discussed above, the mechanism of the combustion of hydrogen sulphide is the most complicated.

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CRITICAL PHENOMENA IN CHAIN REACTIONS WITH DEGENERATE BRANCHING

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I. INTRODUCTION

Limiting (critical) phenomena constitute the clearest and most characteristic feature of branched chain reactions. These phenomena are shown quantitatively in a sharp change in reaction velocity at certain (limiting or critical) values of the external parameters (pressure, temperature, diameter of vessel, etc.). The essential nature of critical phenomena was explained by Semenov's theory of branched chains, supported by a large amount of experimental work by Soviet and foreign scientists. The limits of an autocatalytic chain reaction are certain boundary conditions under which an increase in the concentration of active centres carrying reaction chains becomes possible or impossible. In chain ignitions these conditions are represented by equality of the rates at which the elementary processes of chain branching and termination are occurring. Study of the chain ignition of hydrogen, phosphorus, etc. revealed numerous limiting phenomena (critical pressure, temperature, vessel diameter), and the effect on them of various factors, such as treatment of the walls of the vessel, the action of inert gases and active additions, was investigated.

Besides branched chain reactions, whose development at pressures exceeding the critical value involves ignition of the reactant mixture, slow autocatalytic reactions are known, among them the oxidation of hydrocarbons and other organic substances in both gas and liquid phases. These slow autocatalytic processes were termed by Semenov chain reactions with degenerate branching (or reactions of degenerate chain explosion) [1,2].

According to the theory of degenerate branching, the explanation of the peculiarities of slow oxidation is that, in the course of such reactions, radicals are involved only in the elementary processes of chain propagation and termination, i.e. that the main chain "develops at the normal rate (very rapidly) and is not accompanied by branching in the usually accepted sense" [2]. However, a relatively stable intermediate product is formed in the unbranched primary chain, which, on undergoing some independent reaction (decomposition, oxidation), is responsible for the formation of radicals, i.e. the appearance of secondary chains. "We can regard these secondary chains formally as branches of the primary chain, although a chain of 'degenerate branching' may appear a very considerable time after destruction of the primary chain".

If the number of chains increases by such a mechanism, development of the process is non-stationary:

$$w = \frac{\nu n_0 (k_1 + k_2)}{\varphi} (e^{\varphi t} - 1),$$

where w is the reaction velocity, ν the length of the unbranched chain, n_0 the rate of generation of chains, $\varphi = k_2(\nu - 1) - k_1 = (\nu\delta - 1)/\theta$ is the autocatalytic factor of the reaction, and k_2 and k_1 are the rate constants for decomposition of the intermediate product into radicals and into stable compounds respectively. The parameter $\delta = k_2/(k_2 + k_1)$ is the probability of chain formation involving the stable intermediate, and $\theta = 1/(k_2 + k_1)$ is the mean life of this compound in the reaction. The magnitude of the autocatalytic factor is determined by the low rate of breakdown of the intermediate product into radicals, so that conversion of the starting materials slowly accelerates with time.

The decisive part played by stable intermediate products in the occurrence of slow autocatalytic chain reactions is now supported by a large mass of experimental results. Analysis of kinetic equations [3-6] and also experimental data show that the peculiarities of reactions of this class are determined both by the mechanism of conversion of the intermediate product (radical, molecular, chain) and by the type of chain termination (linear or quadratic).

With variation in the external conditions (diameter of vessel, pressure of mixture, concentration of inhibitor) the autocatalytic factor $\varphi = (\nu\delta - 1)/\theta$ of the degenerate branched chain reaction may be either positive (when $\nu\delta > 1$) or negative (when $\nu\delta < 1$). Hence limiting phenomena should be observed in slow, non-stationary chain reactions, as in chain ignition, if the condition $\nu\delta = 1$ is satisfied [1,2,7-9].

In gas-phase reactions, destruction of chains occurs by the collision of active centres with the surface of the reaction vessel, and the rate of chain termination is proportional to the concentration of radicals (linear termination). In this case the length of the chain ν depends on the diameter and surface state of the reaction vessel and on the pressure of the reactant mixture. The existence of a critical vessel diameter and a critical pressure in the gas-phase oxidation of hydrocarbons has been shown experimentally [10-13].

In the liquid phase the high density of the substance makes the diffusion of active centres to the walls of the reaction vessel difficult, and chain termination occurs by the recombination of radicals (quadratic chain termination). In the quadratic recombination of radicals the length of the chain is independent of any external parameter. Linear chain termination occurs in the liquid phase in the presence of compounds such as phenols, naphthols, amines, etc., which contain a weakly bound hydrogen atom in the hydroxyl or amino-group. The active radicals which effect the chain conversion of the starting materials react with these compounds and are replaced by the corresponding phenoxyl or imino-radicals, which are incapable of chain propagation, so that the chain terminates.

If the rate of chain termination on an inhibitor exceeds the rate of quadratic recombination of radicals, the length of the chain decreases, and induction periods appear in the oxidation. With different inhibitor concentrations, the process of oxidation during the induction period may be stationary ($\varphi < 0$) or may develop autocatalytically ($\varphi > 0$) depending on the length of the chain. The existence of critical inhibitor concentrations, at which a sharp change occurs in the induction period in the liquid-phase oxidation of hydrocarbons, has now been shown experimentally [14,15].

The present Review examines the problem of limiting (critical) phenomena occurring in reactions with degenerate branching of the chains, non-chain consumption of an intermediate product, and linear chain termination.

II. KINETIC EQUATIONS OF A CHAIN REACTION WITH DEGENERATE BRANCHING, LINEAR CHAIN TERMINATION, AND NON-CHAIN CONSUMPTION OF AN INTERMEDIATE PRODUCT

The fundamental mechanism of a chain reaction with degenerate branching comprises the following elementary reactions of radicals r and stable intermediate products x

0) $A+B \xrightarrow{k_0} r$ — chain initiation,

1) $r' + B \xrightarrow{k_1} r + C$
2) $r + A \xrightarrow{k_2} r' + x$ — chain propagation,

3) $x \xrightarrow{k_3} r$ — degenerate branching,
$x \xrightarrow{k_3', k_3''[M]}$ — stable products,

4) $r +$ (wall, inhibitor) $\xrightarrow{g}$ chain termination.

On the basis of this scheme, the variation in concentration of radicals r and the intermediate product x during the reaction is represented by the equations

$$\frac{dr}{dt} = w_0 + k_3 x - gr, \quad (1)$$

$$\frac{dx}{dt} = ar - kx. \quad (2)$$

Chain initiation occurs very slowly in reactions of saturated molecules of the starting materials, its rate being $w_0 = k_0[A][B]$.

The radicals r and r', which are formed in the system, carry reaction chains in which the intermediate product x is formed. The length of the chain is $\nu = a/g$, where $a = k_2[A]$ and g are respectively the kinetic coefficients of chain propagation and termination. The intermediate product x may undergo various reactions during the process. Breakdown of x into radicals (or other reaction) results in an increase in the rate of formation of active centres, i.e. in autocatalysis of the process; the parameter k_3 is the effective rate constant of decomposition of the intermediate product in this way.

The intermediate product can decompose or react with some other molecule M to form stable, valency-saturated compounds, k_3' and $k_3''[M]$ being the effective rate constants of these processes. The parameter $k = k_3 + k_3' + k_3''[M]$ is the overall rate constant for consumption of the intermediate product in the various ways.

In oxidation reactions the intermediate product can be consumed also by a chain mechanism

$$x + r \xrightarrow{k_4} r' + \text{products}.$$

The rate of this process will depend on the concentration of intermediate product and radicals. In the initial stages of conversion, when the concentrations x and r are small, the rate of the chain consumption of the intermediate product $w_{ch} = k_5 xr$ is small, and is ignored in the above scheme.

Eqns. (1) and (2) have the solutions

$$r = \frac{w_0}{(ak_3 - gk)}\left[\frac{(k\lambda_2 + gk - ak_3)}{(\lambda_2 - \lambda_1)}e^{\lambda_1 t} - \frac{(k\lambda_1 + gk - ak_3)}{(\lambda_2 - \lambda_1)}e^{\lambda_2 t} - k\right], \quad (3)$$

$$x = \frac{aw_0}{(ak_3 - gk)}\left[\frac{\lambda_2}{(\lambda_2 - \lambda_1)}e^{\lambda_1 t} - \frac{\lambda_1}{(\lambda_2 - \lambda_1)}e^{\lambda_2 t} - 1\right], \quad (4)$$

where λ_1 and λ_2 are the roots of the characteristic equation $\lambda^2 + (g + k)\lambda - (ak_3 - gk) = 0$ of this system:

$$\lambda_{1,2} = \frac{(g+k)}{2}\left(\pm\sqrt{1 + \frac{4(k_3\nu - k)}{(g+k)(1+k/g)}} - 1\right).$$

If the inequality

$$(k_3\nu - k) \ll (g + k)(1 + k/g), \quad (5)$$

is satisfied, the exponents are

$$\lambda_1 = \frac{(k_3\nu - k)}{(1 + k/g)}, \quad \lambda_2 = -(g + k).$$

The inequality (5) is satisfied if $g \gg k$ or $g \ll k$.

The parameter $1/g = \tau_r$ represents the average life of the radical r, while $1/k = \theta$ is the average life of the intermediate product x. With degenerate branching of the chains, the life of the stable intermediate product should obviously be far longer than that of the radical: $\theta \gg \tau_r$, so that $g \gg k$. If we write $\varphi = k_3\nu - k$, we find that, when $g \gg k$, the exponents are $\lambda_1 = \varphi$ and $\lambda_2 = -g$, and the solutions of Eqns. (1) and (2) become

$$r = \frac{w_0 k_3 \nu}{g\varphi}\left(e^{\varphi t} - \frac{k}{k_3\nu}\right) - \frac{w_0}{g}e^{-gt} = \frac{w_0 k_3 \nu}{g\varphi}\left(e^{\varphi t} - \frac{k}{k_3\nu}\right)_{t \approx 1/g}, \quad (6)$$

$$x = \frac{\nu w_0}{\varphi}(e^{\varphi t} - 1) + \frac{\nu w_0}{g}e^{-gt} = \frac{\nu w_0}{\varphi}(e^{\varphi t} - 1)_{t \approx 1/g}. \quad (7)$$

The solutions (6) and (7) are evidently valid when $dr/dt = 0$, i.e. if the concentration of radicals can be regarded as quasistationary.

Inequality (5) is a condition of quasistationary character either in relation to the concentration of radicals ($dr/dt = 0$), when $g \gg k$, or for the concentration of the intermediate product, when its life θ in the reaction is far shorter than the life of the radicals τ_r, i.e. when $g \ll k$.

The latter case can obviously occur in branched chain reactions†. The inequality (5) can be satisfied whatever

† Fresh results have recently been obtained on the mechanism of branching in chain ignitions [16]. These indicate that the increase in the number of active centres in branched chain reactions is a consequence of the transformation of excited saturated molecules x^*, which are formed in the strongly exothermic stage of chain propagation, and concentrate the heat of reaction in the excitation of vibrational and rotational degrees of freedom.

In the oxidation of hydrogen, for example, chain branching occurs in the reactions

$$H + O_2 \rightarrow HO_2^*,$$
$$HO_2^* \rightarrow HO + O.$$

When $k \gg g$ and condition (5) applies, the concentration of x^* can be regarded as quasistationary, and Eqns. (1) and (2) as equivalent to the equation

$$\frac{dr}{dt} = w_0 + (a\delta^* - g)r = w_0 + (f - g)r,$$

where δ^* is the probability of radical formation from an excited molecule x^*, and $f = a\delta^*$ is the kinetic coefficient of chain branching.

the relationship among the kinetic constants a, k_3, g, and k, if the system is close to a limit, when $k_3\nu \to k$, i.e. $\lambda_1 \to 0$. However, it can be satisfied also if the system is remote from a limit, when $k_3\nu > k$. This case has already been discussed[3] for the degenerate branching of chains.

In degenerate chain branching ($g \gg k$) the condition of quasistationarity with respect to the concentration of radiclas is given by the inequality

$$k_3\nu - k \ll g \quad \text{or} \quad k_3\nu \ll g,$$

if the reaction system is remote from the limit, when $k_3\nu > k$. This inequality can be written[3]

$$\nu \ll \frac{\theta}{\tau_r} \quad \text{or} \quad \nu \ll \sqrt{\frac{\theta}{\tau_m}}, \qquad (5')$$

where $\tau_m = 1/a$ is the life of a radical in the reaction of chain propagation. If $\tau_r \leq 1$ s, while $\theta \simeq 10^3$–10^6 s, which corresponds to the average life of stable intermediate products — aldehydes, hydroperoxides — in the autoxidation of hydrocarbons, condition (5′) is valid with a chain length of $\nu = 10^3$–10^6 steps. In the autoxidation of hydrocarbons the chain length ν is far smaller than this value.

In the analysis of the kinetic equations of chain reactions with degenerate branching it will henceforward be assumed that the condition of quasistationarity is satisfied for the concentration of radicals.

1. Limiting Condition of a Chain Reaction with Degenerate Branching

It is evident from Eqns. (3) and (4) and Eqns. (6) and (7) that the concentrations of radicals r and of the reaction product x will increase with time, i.e. that the process will be autocatalytic, provided that $k_3\nu > k$ ($\lambda_1 > 0$, $\varphi > 0$).

When $k_3\nu < k$ ($\varphi < 0$, $\lambda_1 < 0$) the concentrations of x and r, and hence the reaction velocity $-dA/dt = ar$, will, after a certain time $t \simeq 1/|\varphi|$, become constant:

$$r \to \frac{w_0 k}{g|\varphi|}, \qquad (8)$$

$$x \to \frac{\nu w_0}{|\varphi|}. \qquad (9)$$

The possibility of a chain reaction with degenerate branching passing into a "degenerate unbranched stage" when limiting conditions are reached has been demonstrated previously[3].

The equality $k_3\nu = k$ is the condition for a process to pass from autocatalysis to a steady state. The parameter $\delta = k_3/k$ is none other than the "probability of formation... of a chain when one molecule of intermediate product is involved, i.e. a parameter (formally identical with the previous δ) defining the probability that a chain will branch at a given step" [2].

Thus if a stable intermediate product leads to the formation of active centres in a chain reaction, the limiting condition at which this reaction will be autocatalytic is $\nu\delta = 1$, when ν intermediate product molecules formed in the primary chain yield one secondary chain on further reaction.

Since $\nu = 1/\beta$, the limiting condition is that the probabilities of termination β and of degenerate branching of the chain should be equal: $\beta = \delta$.

2. Autocatalytic Factor in a Chain Reaction with Degenerate Branching and Transition through Limiting Values of the Parameters

The autocatalytic factor in a chain reaction with degenerate branching is the difference between the kinetic coefficients $k_3\nu$ and k, which represent respectively the rate of formation of intermediate product in those chains which have arisen from its breakdown into radicals $k_3 x\nu$ and the total rate of consumption of the intermediate product in the reaction kx:

$$\varphi = k_3\nu - k = k_3\nu(1 - 1/\nu\delta).$$

The expression for φ can be written

$$\varphi = k_3\nu(1 - \nu_{cr}/\nu) = k_3\nu\psi, \qquad (10)$$

where $\psi = 1 - \nu_{cr}/\nu$ and $\nu_{cr} = 1/\delta$ is the chain length at which the autocatalytic factor is zero.

In the liquid-phase oxidation of hydrocarbons the chain length can be varied by additions of inhibitors InH:

$$\nu = k_2[RH]/k_i[InH],$$

where k_2 and k_i are the rate constants for reaction of $RO_2^{\cdot}$ radicals with the hydrocarbon RH and with the inhibitor respectively. We then have $\psi = 1 - [InH]_{cr}/[InH]$.

In the gas-phase oxidation of hydrocarbons, chain termination takes place on the wall of the reaction vessel. The termination rate constant g depends on the diameter of the vessel (kinetic region) and on the pressure of the mixture and the diameter (diffusion region of chain termination).

In gas-phase reactions the rate of chain propagation will depend on the pressure of the mixture, since $a = k_2[RH] = k_2 N\gamma p$, where N is the number of molecules at pressure $p = 1$ mmHg and the temperature of the reaction vessel, γ is the mole fraction of the reactant in the gaseous mixture, and p is the total pressure of the reaction mixture.

If chain termination is determined by the probability of the capture of radicals by the surface of the reaction vessel ($\epsilon_r < 1$, kinetic region of chain termination), we have $g = \epsilon_r u_r/d$, where u_r is the mean thermal velocity of a molecule and d the diameter of the vessel. The chain length in gas-phase oxidation will depend on the pressure of the mixture and the diameter of the vessel:

$$\nu = a/g = \frac{k_2 N\gamma}{u_r \epsilon_r} pd.$$

In this case $\psi = 1 - p_{cr}/p$ for variation of the pressure of the mixture in a vessel of given diameter, and $\psi = 1 - d_{cr}/d$ for variation of the diameter of the vessel at constant pressure.

It follows from Eqn. (10) that, with degenerate chain branching, the autocatalytic factor is determined by the rate constant for decomposition of the intermediate product into radicals k_3 and by the length of the chain ν, and depends on ψ, which measures how far the reaction system is from the limit under given experimental conditions (e.g. how much less is the inhibitor concentration [InH], or how much higher, when $\psi > 0$, is the pressure of the mixture p, than the corresponding limiting values).

In a branched chain reaction the autocatalytic factor is given by the difference between the kinetic coefficents of chain branching f and chain termination g:

$$\varphi_{br} = f - g = f(1 - f/g) = f\psi.$$

In the oxidation of hydrogen above the lower limit in the kinetic region of chain termination ($\epsilon < 1$), the autocatalytic factor is

$$\varphi_{br} = 2a_2(1 - p_{cr}/p) = 2a_2\psi, \quad (11)$$

where $\psi = 1 - p_{cr}/p$, $f = 2k_2[O_2] = 2a_2$, and k_2 is the rate constant of the chain-branching reaction $H + O_2 \xrightarrow{k_2} HO^{\cdot} + {}^{\cdot}O^{\cdot}$. It is seen from Eqns. (10) and (11) that the autocatalytic factors of a branched reaction and of a reaction with degenerate branching are proportional to the rate constant (a_2, k_3) of the process in which the number of active centres increases.

In branched chain reactions the increase in the number of active centres is determined by rapid reactions of radicals with saturated molecules. In such processes the transition from a slow steady-state reaction, involving a negligible rate of initiation of chains (when $\varphi < 0$), to a rapid autocatalytic process (when $\varphi > 0$) is very sharp, with little departure of the external parameters from the critical values, i.e. with a very low value of ψ.

The consumption of the starting materials in the chain ignition of hydrogen is described by the formulae

$$\Delta[O_2] = \frac{n_0}{4a_2\psi} e^{\varphi t} \text{ when } \varphi > 0 \text{ and } t > \frac{1}{\varphi},$$

$$\Delta[O_2] = n_0 t\left(1 + \frac{1}{2|\psi|}\right) \text{ when } \varphi < 0,$$

where $\Delta[O_2] = [O_2]_0 - [O_2]_t$. When $\varphi > 0$, the time t_1 during which the amount $\Delta[O_2]$ of oxygen is used up is

$$t_1 = \frac{2.3 \log A}{\varphi} = \frac{2.3 \log A}{f\psi}, \quad (12)$$

where

$$\varphi = 2a_2\psi = f\psi, \; A = \frac{4a_2\psi^2\Delta[O_2]}{n_0}.$$

When $\varphi < 0$, the time t_2 during which the oxygen concentration falls by $\Delta[O_2]$ is

$$t_2 = \frac{\Delta[O_2] \cdot 2|\psi|}{n_0 \cdot (1 + 2|\psi|)} \quad (13)$$

The ratio t_2/t_1 gives the factor by which the time for a definite consumption of the starting materials $\Delta[O_2]$ increases on passing from $\varphi > 0$ to $\varphi < 0$:

$$t_2/t_1 = C\frac{f}{n_0}, \quad (14)$$

in which

$$C = \frac{\Delta[O_2]\psi^2}{1.15(1 + 2|\psi|)\log A}.$$

In a stoichiometric mixture of hydrogen and oxygen[9] at 800°K and p_{cr} = 7.6 mmHg, we have $a_2 = 310\ s^{-1}$. At the pressure $p_1 = 1.1p_{cr}$, i.e. with $\psi = 0.1$, the autocatalytic factor is $\varphi_{br} = 62\ s^{-1}$, and the time required for 10% of the oxygen to be consumed is $t_1 = 0.2$ s from Eqn. (12). At the pressure $p_1 = 0.9p_{cr}$ ($\psi = -0.1$) the time $t_2 = 3000$ s‡. Thus for a change in pressure of 20%, from $1.1p_{cr}$ to $0.9p_{cr}$, the reaction time increases by a factor of $t_2/t_1 = 1.5 \times 10^4$.

‡ The rate constant of chain initiation in the oxidation of hydrogen[9] is $k_0 \simeq 10^{-22}$ at 800°K. For a stoichiometric mixture of oxygen and hydrogen at 7.6 mmHg the rate of initiation is $n_0 = 10^{-22}[H_2][O_2] = 3.0 \times 10^{-10}$ M s^{-1}.

With degenerate branching of the chains, autocatalysis of a reaction is determined by the rate of formation of primary radicals from molecular intermediate products.

In the oxidation of hydrocarbons the rate constant for decomposition of the hydroperoxide into radicals is $k_3 = 10^{-3}$–$10^{-6}\ s^{-1}$; the autocatalytic factor in these reactions, many orders of magnitude smaller than φ_{br}, is therefore quite remote from the limit ($\psi \to 1$) and thus close to the limit ($\psi \to 0$). This is the reason for the slow increase in rate of a chain reaction with degenerate branching and the less sharp transition through the limiting values of the external parameters.

"Long before critical conditions are approached, the increase in rate is so slow that we find it difficult to fix the sharpness of the transition from complete absence of reaction when $\delta - \beta < 0$ to autocatalysis when $\delta - \beta > 0$". [1]

The variation in reaction time on passing through limiting values of the parameters in the case of degenerate chain branching can be analysed in a similar manner to that used for the branched chain oxidation of hydrogen. The starting materials are consumed in the chain process at the rate $-d[RH]/dt = ar$, where $a = k_2[RH]$, in which k_2 is the rate constant of chain propagation. If the reaction is autocatalytic ($\varphi > 0$), it follows from Eqn. (6) that, after a certain time $t \simeq 1/\varphi$, the variation in radical concentration is described by the equation

$$r = \frac{w_0}{g\psi} e^{\varphi t}.$$

In this case, integration of the equation for the consumption of hydrocarbon with the initial conditions [RH] = $= [RH]_0$ at $t = 0$ leads to the expression

$$\Delta[RH] = \frac{w_0}{k_3\psi^2}(e^{\varphi t} - 1),$$

which is valid when the extent of conversion of the starting materials is small.

Hence the time required for an amount $\Delta[RH]$ of the starting materials to be consumed in an autocatalytic process is

$$t_1 = \frac{2.3 \log A}{\varphi} = \frac{2.3\,\delta(1 - \psi)\log A}{k_3\psi}, \quad (12')$$

where

$$A = \frac{\Delta[RH] \cdot k_3\psi^2}{w_0} + 1$$

and from Eqn. (10)

$$\nu_{\varphi > 0} = \frac{1}{\delta(1 - \psi)}.$$

The variation in radical concentration during the steady state of the process ($\varphi < 0$) is described by Eqn. (8). In this case $\Delta[RH]$ increases with time according to the equation

$$\Delta[RH] = \frac{w_0(1 + |\psi|)\nu_{\varphi<0}}{|\psi|} t_2$$

and the time t_2 for consumption of an amount $\Delta[RH]$ of the starting materials under steady-state conditions of the process is

$$t_2 = \frac{\Delta[RH] \cdot \delta|\psi|}{w_0}, \quad (13')$$

where $\nu_{\varphi<0} = 1/\delta(1 + |\psi|)$ from Eqn. (10).

The change in reaction time on passing through $\varphi = 0$ is given by the ratio

$$t_2/t_1 = C\frac{k_3}{w_0}, \qquad (14')$$

where

$$C = \frac{\psi^3\Delta\,[RH]}{(1-|\psi|)2.3\log A}.$$

Eqns. (12) and (12'), (13) and (13'), and (14) and (14') for the dependence of reaction time on kinetic constants with branching and with degenerate chain branching are analogous to one another.

It follows from Eqns. (14) and (14') that the abruptness of the change in reaction time on passing from autocatalytic to steady-state conditions depends on the relationship between the rate constant for chain branching f (or degenerate branching k_3) and the rate of initiation of chains n_0 (w_0).

Table 1 gives for comparison values of t_1, t_2, and t_2/t_1 found for the oxidation of hydrogen and calculated from Eqns. (12')–(14') for a reaction with degenerate chain branching and different values of the rate constant for dissociation of the intermediate product into radicals. In Table 1 the times t_1 and t_2 relate to the consumption of 10 mole % of the starting materials respectively at $\psi = 0.1$ and $\psi = -0.1$, the rate of initiation of chains is $w_0 = 3\times 10^{-10}$ M s^{-1}, $\delta = 1$, and the concentration of the starting materials is $[RH]_0 = 0.002$ M (in the gas phase this concentration corresponds to 100 mmHg at 423°C).

The calculations show that, in slow non-stationary reactions, a quite abrupt transition through $\varphi = 0$ will be observed provided that the ratio $k_3/w_0 \geq 10^7$ litres mole^{-1}. With $k_3/w_0 \leq 10^6$ no significant change should occur in the reaction time on passing through $\varphi = 0$, and limiting phenomena are not observed. It is obvious that critical phenomena in periodic processes can be observed in sufficently rapid reactions, when $k_3 \simeq 10^{-2} - 10^{-3}$ s^{-1}.

With small values of $k_3 \simeq 10^{-5} - 10^{-6}$ s^{-1} for the rate constant of breakdown of the intermediate product into radicals, even if the rate of initiation is very small (e.g. $w_0 = 10^{-12}$–10^{-13} M s^{-1}) and the ratio t_2/t_1 is large, the absolute values of t_2 and t_1 are so large that it is not possible to study such a process in the vicinity of the limit.

III. CRITICAL PHENOMENA IN THE GAS-PHASE OXIDATION OF HYDROCARBONS

Autoxidation of hydrocarbons in the gas phase occurs at temperatures above 200°C and pressures from a few millimetres of mercury to atmospheric. At such high temperatures and low densities of the hydrocarbon, the main reaction of the peroxy-radical is isomerisation and decomposition with formation of a molecule of a valency-saturated compound and another radical:

$$RO_2^{\cdot} \rightarrow R'CHO + R''O^{\cdot},$$
$$R''O^{\cdot} + RH \rightarrow R''OH + R^{\cdot},$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}.$$

Chain propagation with formation of a hydroperoxide is characteristic of liquid-phase oxidation, whereas in the gas phase it occurs at low temperatures (below 300°C).

Only traces of peroxy-compounds (mainly in the form of hydrogen peroxide, a secondary product) are detected in the products of the autoxidation of hydrocarbons in the gas phase above 300°C, and the only intermediate products are aldehydes [17–24]. The concentration of aldehydes reaches a high value during the reaction. In the oxidation of methane (p_{CH_4} = 110 mmHg at 491.5°C), for example, the maximum concentration of formaldehyde reaches 0.45 mole % of the initial hydrocarbon [21] ($[CH_2O] = 6\times 10^{15}$ cm^{-3}). In the oxidation of propane ($p_{C_3H_8}$ = 116 mmHg at 350°C) the formaldehyde concentration is p_{CH_2O} = 11.5 mmHg ($[CH_2O] = 1.5\times 10^{17}$ cm^{-3}) and that of acetaldehyde p_{CH_3CHO} = 4.5 mmHg ($[CH_3CHO] = 5.8\times 10^{16}$ cm^{-3}). [19] The concentration of radicals in the gas-phase oxidation of hydrocarbons is lower than the limit of sensitivity of modern methods of measurement: $r < 10^{13}$ cm^{-3}. Thus in slow, non-stationary oxidations of hydrocarbons, the concentration of stable intermediate products x is many orders of magnitude greater than the concentration of radicals r:

$$\frac{[RCHO]}{[RO_2]} = \frac{x}{r} > 10^3.$$

It follows from Eqns. (6) and (7) that the concentration ratio of radicals to intermediate product x, with quasi-stationary conditions for the concentration of radicals (when $t > 1/\varphi$), is

$$\frac{x}{r} = \frac{g}{k_3} \gg 1.$$

This is the relationship between the concentrations of stable intermediate products and radicals which is observed in actual processes.

It has now been shown by various methods [22–25] that, in the gas-phase oxidation of hydrocarbons, aldehydes are the only intermediate products involved in the degenerate branching of chains.

The most probable mechanism of degenerate branching is oxidation of the aldehydes according to the equation

$$(3)\ R'CHO + O_2 \rightarrow R'CO^{\cdot} + HO_2^{\cdot} - Q.$$

In a stoichiometric mixture of methane and oxygen at a total pressure of 235 mmHg and at 423°C, the rate of formation of radicals due to oxidation of the intermediate product (formaldehyde) is [22]

$$w_{\text{deg br}} \simeq f\times 10^{-10}\exp(-32\,000/RT)[O_2][CH_2O] \simeq 2\times 10^{-4}[CH_2O],$$

where $f = 10^{-2}$ is the steric factor.

Under these experimental conditions the rate of chain initiation is

$$w_0 \simeq 10^{-10}\exp(-55\,000/RT)[O_2][CH_4] \simeq 10^{-11}\ \text{M s}^{-1}.$$

Consequently the reaction is characterised by the ratio $k_3/w_0 \simeq 10^7$ litres mole^{-1}, where $k_3 = 2\times 10^{-4}$ s^{-1} is the effective rate constant of radical formation by oxidation of

TABLE 1. Abruptness of transition through limiting values of parameters in branched chain and degenerate branched reactions.

	Rate constant f or k_3, s^{-1}	f/n_0 and k_3/w_0	t_1	t_2	t_2/t_1
Oxidation of hydrogen	6.2×10^2	2×10^{13}	0.2 s	3×10^3 s	1.5×10^4
Degenerate branched reaction	$3\cdot 10^{-2}$	10^8	1.32 h	55 h	40
	$3\cdot 10^{-3}$	10^7	7.5 »	55 »	7
	$3\cdot 10^{-4}$	10^6	26 »	55 »	2
	$3\cdot 10^{-5}$	10^5	46 »	55 »	1.2
	$3\cdot 10^{-6}$	10^4	50 »	55 »	1.1

the intermediate product. According to the above calculations, with this ratio the transition through the limiting conditions should be far less abrupt than in the oxidation of hydrogen, as is confirmed by experimental results [13]. In the oxidation of methane at 423°C with p_{O_2} = 157 mmHg and p_{CH_4} = 78 mmHg, the life of the radicals $CH_3^{\cdot}$ and $^{\cdot}OH$ in the reactions of chain propagation is [9] $\tau_m = 5 \times 10^{-6}$ s. If the length of the chain is $\nu \simeq 100$ steps [26], the life of the chain is $\tau_\gamma = \tau_m \nu \simeq 5 \times 10^{-4}$ s. However, the average appearance time of a radical (i.e. of a secondary chain) by the breakdown of ν = 100 aldehyde molecules formed in the primary chain is $1/k_3\nu \simeq 50$ s. Hence it follows that, in processes of slow oxidation, propagation of chain — from the moment it is formed until it is destroyed — occupies a far shorter time than does formation of a fresh chain by breakdown of the intermediate product into radicals [2].

Apart from being used up in degenerate chain branching, the aldehydes are involved in several other reactions, which do not result in the formation of radicals. In the oxidation of methane, for example, it is supposed that formaldehyde may decompose on the walls of the reaction vessel [21]:

$$CH_2O \xrightarrow{\text{wall}} \text{products}.$$

Thus the probability of degenerate branching of the chains is less than unity ($\delta < 1$). In later stages of the reaction the aldehydes are consumed by a chain mechanism, e.g.

$$CH_2O + {}^{\cdot}OH \rightarrow H_2O + HCO^{\cdot}.$$

It has been shown [3] that, with consumption of the intermediate product by a chain mechanism and linear termination of chains, a steady-state concentration of the intermediate product is established, and the rate of oxidation becomes constant. After the induction period is over, however, the chain consumption of aldehydes in the gas-phase oxidation of hydrocarbons, and of hydroperoxides in the liquid-phase process, proceeds at an appreciable rate with a high radical concentration. In the early stages of conversion, therefore, the chain consumption of intermediate products can be disregarded. In the oxidation of methane it has been shown [25] that $\varphi\tau$ is approximately constant during the initial stages of the reaction (up to 10% conversion), which is consistent with a mechanism of the process which ignores the chain consumption of formaldehyde.

The gas-phase oxidation of hydrocarbons is greatly dependent on the state and treatment of the walls of the reaction vessel. The reaction velocity increases with increase in the diameter of the vessel and in the pressure of an inert gas [5,10,13]. This indicates that the destruction of active centres occurs on the surface of the reaction vessel. It has been established [5] that, in the oxidation of methane, chain termination takes place in the region of diffusion-controlled kinetics.

With chain termination on the surface of the vessel, a critical diameter d_{cr} and a critical pressure p_{cr} should be observed, their values being determined from the condition $\varphi = 0$. The existence of these critical parameters has been found in the gas-phase oxidation of various compounds. A study [10] of the oxidation of acetylene under flow conditions at 320°C and 400 mmHg in tubes of different diameters showed that the reaction occurred slowly at 2 and 4 mm, and quite rapidly at 6, 10, and 20 mm diameter. A change in diameter of the vessel from 4 to 6 mm produced a thirtyfold increase in reaction velocity. Thus the experimental results indicate the presence of a critical diameter $d_{cr} \simeq 4$ mm.

The existence of critical conditions d_{cr}, p_{cr}, and t_{cr} was found in the oxidation of ethane [11]. The increase in pressure during the process (Fig. 1), in a vessel of diameter 5 mm at 708°C and pressures of 134, 98, and 94.5 mmHg, was represented by the exponential law

$$\Delta p = N(e^{\varphi t} - 1).$$

The kinetic curves changed from concave to convex at pressures of 92–60 mmHg, and the variation in pressure was described by the equation to a steady-state process $\Delta p = A(1 - e^{-kt})$. A change in shape of the kinetic curves representing the autocatalytic and the steady-state process was observed with change in the experimental temperature and in the diameter of the vessel. In all cases the $\Delta p_{max} - p_0$ relationship changed abruptly at the critical values of the diameter, the pressure, and the temperature (Fig. 2). It was assumed [11] that, in the oxidation of ethane, the homogeneous reaction was accompanied by oxidation on the walls of the vessel, which prevented a sharper development of critical reaction conditions.

Critical phenomena are clearly evident in the oxidation of arsine [12]. A stoichiometric mixture of arsine and oxygen could remain in a spherical vessel of diameter d = = 10 cm at 50°C without change for an indefinite time if the pressure was lower than p_{cr} = 143 mmHg. At higher pressures the mixture slowly reacted, the pressure falling and As_2O_3 being deposited on the walls of the vessel. Reaction ceased when the pressure had fallen to a certain value p_{cr}. At constant temperature and pressure a critical diameter d_{cr} was shown to exist, which was linked with p_{cr} by the constancy of their product $p_{cr}d_{cr}$, a relationship known from the kinetics of chain ignitions. At a pressure of 94 mmHg, for example, the critical diameter is d_{cr} = = 15 cm, and at 143 mmHg it is 10 cm. The temperature dependence of the critical diameter is given by the relation $\log d_{cr} = A/T + B$. Thus the temperature dependence of d_{cr} exhibits the same regularities as does that of branched chain reactions.

An investigation has been made [13] of the effect of the diameter of the vessel on the rate of oxidation of a number of saturated and unsaturated hydrocarbons (methane, ethane, propane, ethylene, propene, and acetylene). Fig. 3 shown the dependence on vessel diameter of the time

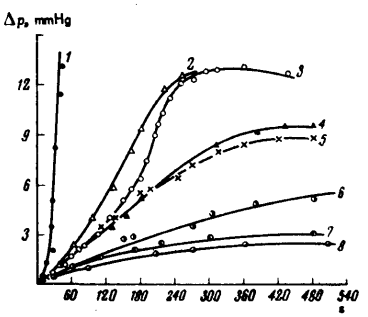


Fig. 1. Kinetic curves of increase in pressure in the oxidation of ethane (in a $C_2H_6 + 3.5O_2$ mixture at 708°C in a quartz vessel with d = 5 mm) at various initial pressures (mmHg) of the reactant mixture:
1) 134; 2) 98; 3) 94.5; 4) 91.5; 5) 92; 6) 90.5; 7) 80; 8) 60.

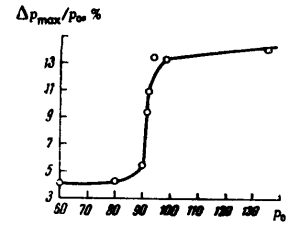


Fig. 2. Dependence of maximum increase in pressure in the oxidation of ethane on the initial pressure of the reactant mixture ($C_2H_6 + 3.5O_2$) at 700°C with d = 5 mm.

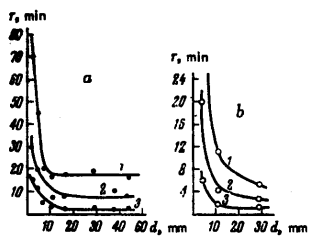


Fig. 3. Dependence of induction period on diameter of vessel in oxidation of: *a*) propene in $C_3H_6 + 3O_2$ mixture at 360°C; *b*) methane in equimolecular mixture with oxygen at 530°C; at various initial pressures (mmHg): 1) 150; 2) 200; 3) 300.

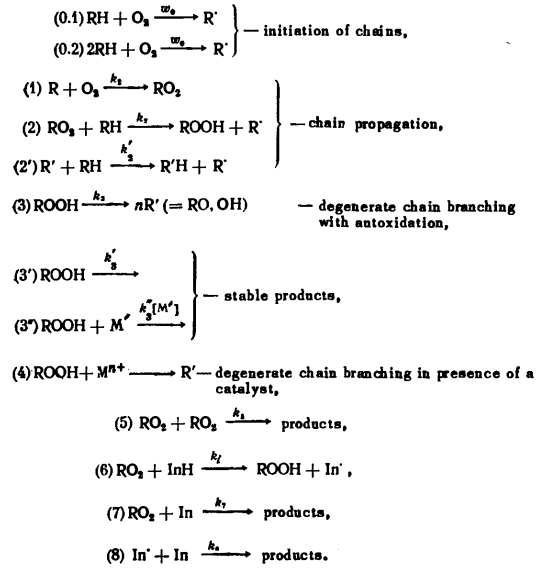
required for the reaction velocity to reach its maximum value (the induction period) in the oxidation of methane and propene. It is seen that a more or less sharp break occurs at a certain diameter, below which the reaction velocity falls sharply.

IV. PHENOMENON OF A CRITICAL INHIBITOR CONCENTRATION IN THE LIQUID-PHASE OXIDATION OF HYDROCARBONS IN BATCHES

1. Kinetics of the Inhibited Oxidation of Hydrocarbons from the Viewpoint of Limiting Phenomena

From a consideration of the fundamental mechanism of the oxidation of hydrocarbons with chain termination on an inhibitor, Semenov showed that a critical inhibitor concentration $[InH]_{cr}$ should exist, above which the process will be stationary, i.e. very slow, and below which it should be autocatalytic [9].

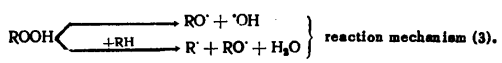
According to present-day ideas, the oxidation of a hydrocarbon in the presence of an inhibitor comprises the following set of elementary stages



In this scheme R′ denotes a primary radical RO or OH, formed by the breakdown of a hydroperoxide, and M′ is a sulphide, phosphite, etc., which decomposes hydroperoxides with the formation of valency-saturated compounds. Many quantitative data are now available on the rates of the elementary reactions in liquid-phase oxidation. The most probable mechanism of chain initiation is the bimolecular reaction (0.1) for a hydrocarbon of bond energy $Q_{RH} > > 90$ kcal mole^{-1} and the termolecular reaction (0.2) for a hydrocarbon of bond energy $Q_{R-H} < 90$ kcal mole^{-1}. [27] The value of w_0 is 10^{-11}–10^{-8} M s^{-1} depending on the temperature and the nature of the hydrocarbon [27,28].

The autocatalytic character of the liquid-phase oxidation of hydrocarbons is associated with the formation of radicals by the breakdown of hydroperoxides, the stable intermediate products formed in the reaction of chain propagation. Comparison, by a kinetic tracer method, of the rates of consumption of hydroperoxides and of accumulation of the final products (ketones, alcohols, acids) in the oxidation of n-decane [29] (at 140°C), and also in the oxidation of cyclohexane [30] (155°C) has demonstrated rigorously that hydroperoxides are the primary and practically the only intermediate products in the liquid-phase autoxidation of hydrocarbons.

A great amount of work has been done on the mechanism of the dissociation of hydroperoxides into radicals and the part played by this process in accelerating oxidation processes (degenerate chain branching). Radicals are formed by the unimolecular breakdown of hydroperoxides at the weak O–O bond and as a result of a bimolecular reaction with the hydrocarbon [31–33]:



The experimental data in Table 2 show that at 100–140°C, when the liquid-phase autoxidation of hydrocarbons takes place at a measurable rate, the radical decomposition constant of the hydroperoxides is $k_3 \simeq 10^{-6}$–10^{-4} s^{-1}.

TABLE 2. Rate constants for the dissociation of hydroperoxides into radicals.

Hydroperoxide	k_3, s^{-1}	k_3, s^{-1}, at 100–140°C	Ref.
n-Decyl	$6\cdot10^{8}\exp(-24\,800/RT)$	$1.5\cdot10^{-6}$—$5.0\cdot10^{-5}$	34
Cyclohexyl	$1.2\cdot10^{13}\exp(-34\,000/RT)$	$1.2\cdot10^{-7}$—$4\cdot10^{-6}$	35
Decahydronaphthyl	$8.5\cdot10^{13}\exp(-32\,100/RT)$	$1.2\cdot10^{-5}$—$7.9\cdot10^{-5}$	36

The dissociation of a hydroperoxide into radicals can be initiated by a metal of variable valency (by a cobalt, copper, manganese, nickel, or iron salt). Radical formation in the presence of such a metal in glacial acetic acid[37] results from the reactions

$$ROOH + M^{n+} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} [ROOH \cdot M^{n+}],$$

$$[ROOH \cdot M^{n+}] + M^{n+} \xrightarrow{k_c} RO^{\cdot} + M^{n+} + M^{3+}(OH),$$

$$[ROOH \cdot M^{n+}] + M^{3+}(OH) \xrightarrow{k_d} RO_2^{\cdot} + 2M^{n+} + H_2O.$$

It follows from the stoichiometric equation for this process

$$2ROOH \rightarrow RO^{\cdot} + RO_2^{\cdot} + H_2O,$$

that one radical is formed per hydroperoxide molecule decomposed. The rate of breakdown of the hydroperoxide in the presence of a metal of variable valency is proportional to the hydroperoxide concentration:

$$-d[ROOH]/dt = k_4[ROOH],$$

where $k_4 = 2k_c k_a[M^{n+}]^2/k_b$ at low catalyst concentrations $[M^{n+}]$, and $k_4 = k_a[M^{n+}]$ at high concentrations thereof. Under the actual conditions of the catalysed oxidation of hydrocarbons (tetrahydronaphthalene[38], ethylbenzene[39], n-decane[40], cyclohexane[41]) in the presence of salts of metals of variable valency, $k_4 = 0.001$–$0.1\ s^{-1}$.

In the mechanism of the breakdown of hydroperoxides, reactions in which stable molecules are formed directly — reactions (3′) and (3″) — must be taken into account as well as those leading to the production of radicals. The formation of valency-saturated compounds by the unimolecular decomposition of substances in the liquid phase is associated with a "cage effect", consisting in recombination of a proportion of the radicals without their escaping from the "cage" of the solvent[42]. For example, the hydroperoxide of n-decane in this hydrocarbon as medium at 130°C breaks down into radicals at a rate, measured from the consumption of inhibitor, which is 0.6 of the total rate of decomposition: i.e. 1.2 radicals are formed per hydroperoxide molecule decomposed. The remaining 0.4 of the total rate of decomposition represents reactions in which molecular products are formed[43].

A hydroperoxide breaks down without radical formation on reaction with alkyl and aryl sulphides[44,45], selenium compounds[46], and phosphoric esters[47–49]:

$$(3'')\ ROOH + R'SR \longrightarrow ROH + R'S(O)R.$$

The role of a hydroperoxide in the autocatalysis of oxidation is governed by competition between reactions (3) or (4) and reactions (3′) and (3″), i.e. by the value of $\delta = k_3/k$.

In the liquid phase the diffusion of radicals to the walls of the vessel is made very difficult by the high density of the substance, and liquid-phase oxidation in the absence of inhibitors is characterised by quadratic chain termination with recombination of the radicals. At oxygen pressures of $p_{O_2} \simeq 200$–300 mmHg the concentration of alkyl radicals R$^{\cdot}$ is far lower than that of $RO_2^{\cdot}$ radicals, and therefore chain termination occurs by reaction (5).

The rate constant for the recombination of $RO_2^{\cdot}$ radicals has been measured for various hydrocarbons[50–56], and its value of $k_5 = 10^5$–10^7 litres mole^{-1} s^{-1} is almost independent of temperature ($E_5 \leq 2$ kcal mole^{-1}). In the absence of inhibitor, the variation in radical concentration is given by the equation

$$d[RO_2]/dt = w_0 + nk_3[ROOH] - k_5[RO_2]^2 = 0,$$

from which it follows that the radical concentration is $[RO_2^{\cdot}] = \sqrt{w_i/k_5}$, where $w_i = w_0 + nk_3[ROOH]$ is the rate of initiation of radicals. The length of the chain ν and the rate of oxidation of the hydrocarbon w are

$$\nu = a/g = k_2[RH]/\sqrt{w_i k_5},$$

$$w = k_2[RH]\sqrt{w_i/k_5}.$$

The parameter $g_{qu} = \sqrt{w_i k_5}$ is the effective rate constant for the destruction of $RO_2^{\cdot}$ radicals by quadratic chain termination.

The rate of oxidation of a hydrocarbon is diminished by the presence of an amine, a phenol, or a naphthol, containing an OH, NH_2, or > NH group. Much work has been done on the mechanism of the action of inhibitors and on the kinetics of inhibited oxidation in connection with the practical problems of the stabilisation of various substances (fats, oils, petroleum products, and polymeric materials) against oxidative degradation. Progress in the practical application of antioxidants and in studying the mechanism of their action has been summarised in several reviews and monographs[57–59].

The retardation of oxidation processes in the presence of compounds containing the above groups results from the abstraction of the weakly bound hydrogen by $RO_2^{\cdot}$ radicals with the formation of relatively inactive In$^{\cdot}$ radicals, reaction (i). The parameter $g_{In} = k_i[InH]$ is the kinetic coefficient of the loss of $RO_2^{\cdot}$ radicals in reactions with the inhibitor. The mechanism of the action of inhibitors represented by reaction (i) is supported by kinetic data on the rates of oxidation of hydrocarbons in the presence of inhibitors[61–65], by isotopic[63], spectroscopic[66], and chemiluminescent methods[67], and by several other data[68].

Various methods have been proposed[64,69,70] for measuring the rate constant k_i, which depends on the nature of the inhibitor, the medium (hydrocarbon), and the temperature. Values of $k_i \simeq 10^3$–10^5 litres mole^{-1} s^{-1} have been obtained for inhibitors of varying efficiency. The activation energy for abstraction of a hydrogen atom from an inhibitor molecule by $RO_2^{\cdot}$ radicals is $E_i \simeq 3$–8 kcal mole^{-1}.

The structure and the reactivity of In$^{\cdot}$ radicals have been studied by chemical[71] and physical methods. Most of the recent information on their structure and reactions has been obtained by the electron spin resonance method[72], by means of which In$^{\cdot}$ radicals have been detected in the oxidation of polypropylene in the presence of 1- and 2-naphthols, 4-methyl-2,6-di-t-butylphenol, diphenylamine, and other inhibitors[72,73]. The reaction products from inhibitors under oxidising conditions have been found to include compounds In–RO_2 and In–In, in which the In$^{\cdot}$ radical has either a phenoxy or a quinonoid structure. These compounds could be formed in reactions (7) and (8).[57] If the In$^{\cdot}$ radical is involved in chain termination by reaction (7),

the number of chains m destroyed on one inhibitor molecule exceeds unity ($m \geq 1$).

It has been found that many inhibitors containing one OH or NH_2 group terminate two oxidation chains ($m = 2$), and that bifunctional compounds terminate four oxidation chains ($m = 4$):[67,74,75] i.e. under these conditions the In$^\cdot$ radicals disappear only in reaction (7). The rate constant of this reaction has been determined[76] as $k_7 \simeq 10^9$ litres mole^{-1} s^{-1} for the tetrahydronaphthylperoxy-radical and the phenoxy--radical. Thus this constant is larger than k_i by factors of 10^2–10^4.

The stability of the In$^\cdot$ radical and its ability to react with saturated hydrocarbon molecules

$$(9)\ \mathrm{In}^\cdot + \mathrm{RH} \rightarrow \mathrm{R}^\cdot + \mathrm{InH},$$

vary according to the nature, positions, and number of substituents in the molecule of the initial inhibitor. The rate constant for the abstraction of a hydrogen atom by 2,4,6-tri-t-butylphenoxy-radicals from various hydrocarbons (n-decane, 2,4,6-trimethylheptane, ethylbenzene, cumene) is small ($E_9 \simeq 20$–27 kcal mole^{-1}).[77] In the case of other In$^\cdot$ radicals (in particular from phenol), however, it is supposed that both reaction (9) and

$$(10)\ \mathrm{In}^\cdot + \mathrm{ROOH} \rightarrow \mathrm{InH} + \mathrm{RO}_2^\cdot,$$

are very rapid[63,78,79]. In reactions (9) and (10) the In$^\cdot$ radicals are involved in chain transfer, which substantially lowers the efficiency of the inhibitors. Phenols whose radicals are involved in the chain-transfer processes (9) and (10) are relatively ineffective. The peculiarities of the retardation of oxidation processes by inefficient inhibitors have been analysed[57,63,78,79]. The possibility of various reactions of phenols and amines and their radicals, and hence the overall efficiency of the retardation of an oxidation process by inhibitors, depend on the conditions of oxidation, in particular on the temperature. Above 150°C phenols and amines are consumed mainly by direct oxidation. It is assumed that this process can result in the initiation of chains[45,80]. Little work has been done on the products of the direct oxidation of inhibitors or on their effect on the oxidation of a hydrocarbon.

Here we shall consider the kinetic laws of inhibited oxidation and experimental results on critical concentrations of efficient inhibitors, not involved in any reaction other than those of chain termination. The features of this phenomenon with amines and phenols as inhibitors at high temperatures of 180–220°C, when these compounds undergo reactions other than chain termination, have been discussed in other papers[60,80–84].

According to the above mechanism, the variation in radical concentration is governed by the equations

$$\frac{d[\mathrm{R}]}{dt} = w_0 + k_2[\mathrm{RO}_2][\mathrm{RH}] + k_2'[\mathrm{R}'][\mathrm{RH}] - k_1[\mathrm{R}][\mathrm{O}_2] = 0,$$

$$\frac{d[\mathrm{R}']}{dt} = nk_3[\mathrm{ROOH}] - k_2'[\mathrm{R}'][\mathrm{RH}] = 0,$$

$$\frac{d[\mathrm{RO}_2]}{dt} = k_1[\mathrm{R}][\mathrm{O}_2] - k_2[\mathrm{RO}_2][\mathrm{RH}] - k_i[\mathrm{RO}_2][\mathrm{InH}] - k_7[\mathrm{RO}_2][\mathrm{In}] - k_5[\mathrm{RO}_2]^2 = 0,$$

$$\frac{d[\mathrm{In}^\cdot]}{dt} = k_i[\mathrm{RO}_2][\mathrm{InH}] - k_7[\mathrm{RO}_2][\mathrm{In}] - k_8[\mathrm{In}]^2 = 0.$$

From the last equation it follows that the concentration of In$^\cdot$ radicals can be written

$$[\mathrm{In}] = \frac{k_i[\mathrm{RO}_2][\mathrm{InH}]}{k_7[\mathrm{RO}_2] + k_8[\mathrm{In}]} = \frac{\alpha k_i[\mathrm{InH}]}{k_7},$$

where $\alpha = k_7[\mathrm{RO}_2]/(k_7[\mathrm{RO}_2] + k_8[\mathrm{In}])$ is the probability of chain termination by In$^\cdot$ radicals. Adding up the first three equations, we obtain for the variation in concentration of $RO_2^\cdot$ radicals the equation

$$w_0 + nk_3[\mathrm{ROOH}] = k_i[\mathrm{RO}_2][\mathrm{InH}] + k_7[\mathrm{RO}_2][\mathrm{In}] + k_5[\mathrm{RO}_2]^2 = mk_i[\mathrm{RO}_2][\mathrm{InH}] + k_5[\mathrm{RO}_2]^2, \quad (15)$$

where $m = 1 + \alpha$ is the number of chains destroyed on one inhibitor molecule. With $\alpha = 0$, when the constant k_7 is zero, we have $m = 1$; and with $\alpha = 1$ and $k_8 = 0$, we find that $m = 2$. Thus the parameter m can have values of $2 \geq m \geq 1$.

From Eqn. (15) the concentration of $RO_2^\cdot$ radicals can be expressed

$$[\mathrm{RO}_2^\cdot] = \frac{mk_i[\mathrm{InH}]}{2k_5}\left(\sqrt{1 + \frac{4k_5w_i}{m^2k_i^2[\mathrm{InH}]^2}} - 1\right).$$

When $mk_i[\mathrm{InH}] \ll \sqrt{w_ik_5}$, i.e. when $g_{\mathrm{lin}} \ll g_{\mathrm{qu}}$, the quadratic termination of chains predominates over linear termination, and the inhibitor does not retard the reaction.

If

$$mk_i[\mathrm{InH}] \gg \sqrt{w_ik_5}, \text{ i.e. } g_{\mathrm{lin}} \gg g_{\mathrm{qu}}, \quad (16)$$

the radical concentration is

$$[\mathrm{RO}_2] = \frac{w_i}{mk_i[\mathrm{InH}]} = \frac{w_0 + nk_3[\mathrm{ROOH}]}{mk_i[\mathrm{InH}]}. \quad (17)$$

In this case the chain length $\nu_{\mathrm{inh}} = k_2[\mathrm{RH}]/mk_i[\mathrm{InH}]$ becomes less than the length ν_{qu} in the absence of inhibitor:

$$\frac{k_2[\mathrm{RH}]}{mk_i[\mathrm{InH}]} < \frac{k_2[\mathrm{RH}]}{\sqrt{w_ik_5}}.$$

In the presence of efficient inhibitors, therefore, induction periods appear in the oxidation process right up until the inhibitor is practically completely exhausted, when the relationship (16) ceases to be satisfied. The inequality (16) determines the inhibitor concentration [InH] at which linear termination predominates over quadratic termination[85,86].

This inequality is responsible for the fact that an inhibitor may retard oxidation when introduced at the start of the reaction ($w_i \simeq w_0$), but prove ineffective when introduced at later stages, when the rate of initiation w_i far exceeds the rate of generation of chains w_0. With linear termination of chains on the inhibitor, the variation in hydroperoxide concentration during the reaction is given by the equation

$$\frac{d[\mathrm{ROOH}]}{dt} = (k_2[\mathrm{RH}] + k_i[\mathrm{InH}])\frac{(w_0 + nk_3[\mathrm{ROOH}])}{mk_i[\mathrm{InH}]} - k[\mathrm{ROOH}],$$

which can be written

$$\frac{d[\mathrm{ROOH}]}{dt} = \nu' w_0 + \varphi[\mathrm{ROOH}], \quad (18)$$

where

$$\nu' = \frac{k_2[\mathrm{RH}]}{mk_i[\mathrm{InH}]} + \frac{1}{m} = \nu + \frac{1}{m},$$

is the chain length taking into account the hydroperoxide formed in the chain-termination reaction (i), and $\varphi = k_3n\nu' - k$ is the autocatalytic factor of the process. If ν and φ do not vary with time, integration of Eqn. (18) with the initial conditions $[\mathrm{ROOH}]_0 = 0$ at $t = 0$ leads to the equations

$$[\mathrm{ROOH}] = \frac{\nu' w_0}{\varphi}(e^{\varphi t} - 1) \quad (19)$$

and

$$[RO_2^{\cdot}] = \frac{w_0 k_3 \nu'}{m k_i [InH]\,\varphi}\left(e^{\varphi t} - \frac{k}{n k_3 \nu'}\right). \quad (20)$$

These equations are identical with Eqns. (6) and (7) for the variation in concentration of radicals and of intermediate product obtained on analysing the general scheme of a chain reaction with degenerate branching when $n = 1$ and $g = mk_i[InH]$. Therefore the consumption of hydrocarbon

$$-d[RH]/dt = k_2[RO_2^{\cdot}][RH]. \quad (21)$$

during the induction period of inhibited oxidation should be governed by the relations (12′) and (13′), as well as by Eqn. (14′), which defines the abruptness of the change in induction period on passing through the critical inhibitor concentration.

Fig. 4 (curves *1–3*) illustrates the dependence, calculated from Eqns. (12′) and (13′) of induction period on inhibitor concentration. The time required for 0.01 mole% of the hydrocarbon to be consumed was taken as the end of the induction period; formation of hydroperoxide in the termination reaction was ignored. Calculations were made with experimental values of the elementary rate constants obtained in a study of the liquid-phase oxidation of hydrocarbons: $k_2 = 2.0$ litres mole^{-1} s^{-1}, $k_i = 2 \times 10^5$ litres × × mole^{-1} s^{-1}, $k_3 = 10^{-2}$ (1), 10^{-3} (2), and 10^{-5} (3) s^{-1}, $w_0 = 10^{-10}$ M s^{-1}, [RH] = 5.0 M, $k = k_3$, $m = 1$, and $n = 1$.

Fig. 4 shows that, with the ratio $k_3/w_0 = 10^8$ and 10^7 litres mole^{-1} (curves *1* and *2*), the induction period

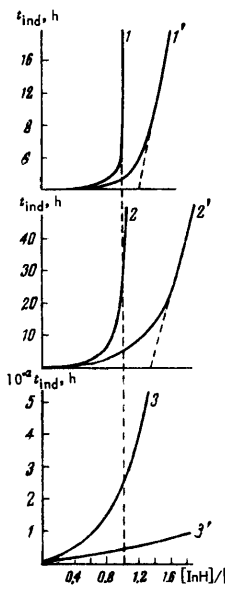


Fig. 4. Dependence of induction period (time required for 0.01% conversion of the hydrocarbon) on inhibitor concentration for different values of the rate constant k_3 (s^{-1}) for dissociation of the hydroperoxide into radicals: 1) and 1′) 10^{-2}; 2) and 2′) 10^{-3}; 3) and 3′) 10^{-5}; 1)–3) inhibitor concentration maintained constant; 1′)–3′) inhibitor used up (calculated values).

increases quite sharply at the critical inhibitor concentration. When the ratio is $k_3/w_0 = 10^5$ litres mole^{-1} (curve *3*), the induction period varies smoothly throughout the concentration range of the inhibitor; limiting phenomena are not found with such ratios of k_3 to w_0.

2. Value of Critical Inhibitor Concentration

The critical concentration of the inhibitor is evaluated from the condition that the autocatalytic factor of the process φ should vanish, i.e. that

$$\nu_{cr} + 1/m = 1/n\delta \quad (22)$$

and is given by

$$[InH]_{cr} = \frac{k_2[RH]\,n\delta}{k_i(m - n\delta)}. \quad (23)$$

According to Eqns. (22) and (23), at values of $n\delta \geqslant m$, oxidation should develop with autocatalysis at any inhibitor concentration — even with very short chains — owing to the hydroperoxide formed in the chain-terminating reaction (*i*). When, however, $\nu \leqslant 1$, reaction of $RO_2^{\cdot}$ radicals with the inhibitor should be accompanied by that of the primary radicals RO and OH (= R′) formed by dissociation of the hydroperoxide. In this case the mechanism of the process should be supplemented by the reactions

$$(i')\ R' + InH \xrightarrow{k_i'} R'H + In^{\cdot},$$

$$(7')\ R' + In \xrightarrow{k_7'} \text{products}.$$

These reactions should yield an alcohol or water, products which do not result in autocatalysis of the process. The occurrence of reactions between the R′ radicals and the inhibitor under oxidation conditions has been demonstrated experimentally [28].

If these reactions take place, and provided that $k_i/k_i' = k_2/k_2' = k_7/k_7'$, the concentrations of the radicals can be written

$$[R'] = \frac{nk_3[ROOH]}{k_2'[RH] + mk_i'[InH]}, \quad [RO_2^{\cdot}] = \frac{w_0 + \gamma n k_3[ROOH]}{mk_i[InH]},$$

where

$$\gamma = \frac{k_2'[RH]}{k_2'[RH] + mk_i'[InH]} = \frac{\nu}{\nu + 1},$$

is the probability of the formation of peroxy-radicals $RO_2^{\cdot}$ from the primary radicals R′, i.e. the probability of propagation of the chain by R′ radicals. In this case we have for m

$$m = 1 + \frac{\alpha(1 + a)}{1 + a\alpha}, \text{ where } a = \frac{k_i'[R']}{k_i[RO_2^{\cdot}]}.$$

Just as in the preceding case $m = 1$ when $\alpha = 0$, and $m = 2$ when $\alpha = 1$.

The autocatalytic factor of the process in Eqns. (19) and (20) becomes $\varphi = k_3 n\gamma(\nu + 1/m) - k$, while the limiting condition is given by

$$(\nu_{cr} + 1/m)\,\gamma_{cr} = \frac{(\nu_{cr} + 1/m)\,\nu_{cr}}{(\nu_{cr} + 1)} = \frac{1}{n\delta}, \quad (22')$$

from which it follows that in general, with various chain lengths taken into account, the critical inhibitor concentration is given by the formula

$$[InH]_{cr} = \frac{k_2[RH]\,n\delta\gamma_{cr}}{k_i(m - \gamma_{cr}n\delta)}. \quad (23')$$

It is seen from Eqn. (22′) that the critical concentration should be finite for any relationship between the parameters $2 \geqslant m \geqslant 1$ and $n\delta \leqslant 2$. We have

$$\nu_{cr} = \frac{1}{2}\left(\frac{1}{n\delta} - \frac{1}{m}\right) + \sqrt{\frac{1}{4}\left(\frac{1}{n\delta} - \frac{1}{m}\right)^2 + \frac{1}{n\delta}},$$

when $n\delta \ll m$, the chain length $\nu_{cr} \gg 1$, $\gamma_{cr} \simeq 1$, and the critical inhibitor concentration is

$$[InH]_{cr} = \frac{k_2[RH]n\delta}{k_i m}.$$

When $n\delta = m$ the critical inhibitor concentration is

$$[InH]_{cr} = \frac{k_2[RH]}{k_i\sqrt{m}}.$$

3. Effect of Inhibitor Consumption on Abruptness of Change in Induction Period on Passing through the Critical Inhibitor Concentration

Eqns. (19) and (20) for the variation in concentration of radicals and hydroperoxide have been obtained on the assumption that the chain length ν and the autocatalytic factor φ remain unchanged during the reaction. This might have been the case if the inhibitor concentration had been maintained constant. However, the chief feature of inhibited oxidation is the consumption of inhibitor, which occurs at the rate

$$-d[InH]/dt = k_i[RO_2][InH] = \frac{w_0 + nk_3[ROOH]}{m}. \qquad (24)$$

If inhibitor is consumed, the effective rate constant of chain termination $g_{1in} = mk_i[InH]$ continuously diminishes, while the chain length and the autocatalytic factor increase, during the reaction.

An analysis has been made[87] of the effect of inhibitor consumption on the sharpness of the transition through $[InH]_{cr}$. The set of equations (15), (18), (21), and (24) for the concentration variation of radicals, intermediate product, inhibitor, and hydrocarbon was solved by numerical integration on an electronic computer. The values chosen for the elementary rate constants were $k_2 = 2.0$ litres × × mole^{-1} s^{-1}, $k_i = 2 \times 10^5$ litres mole^{-1} s^{-1}, $k_5 = 2 \times \times 10^7$ litres mole^{-1} s^{-1}, $w_0 = 10^{-10}$ M s^{-1}, [RH] = 5.0 M, $k_3 = 10^{-2}$–10^{-5} s^{-1}, $m = 1$, $n = 1$, and $k = k_3$. The formation of hydroperoxide by chain termination on the inhibitor was ignored in Eqn. (15).

The data given above showed that the values chosen for the rate constants simulate very closely actual processes of the autoxidation (with $k_3 = 10^{-4}$–10^{-5} s^{-1}) and the catalysed oxidation (with $k_3 = 10^{-2}$–10^{-3} s^{-1}) of hydrocarbons.

Figs. 5 and 6 illustrate kinetic curves for inhibitor consumption at k_3/w_0 ratios of 10^8 and 10^5 litres mole^{-1} (Figs. 5*a* and 6*a*) and the variation in the autocatalytic factor (Figs. 5*b* and 6*b*) during the process. Fig. 4 (curves *1′*–*3′*) gives the dependence of the induction period on the initial inhibitor concentration in this process. The end of the induction period is taken to be the time at which 0.01 mole % of the hydrocarbon has disappeared, when the inhibitor has already been completely exhausted. Figs. 5*b* and 6*b* show that the autocatalytic factor increases steadily during the process from negative values at $[InH] > [InH]_{cr}$ to positive values at $[InH] < [InH]_{cr}$.

At the ratio $k_3/w_0 = 10^8$ the inhibitor is consumed autocatalytically during the induction period (Fig. 5*a*) when

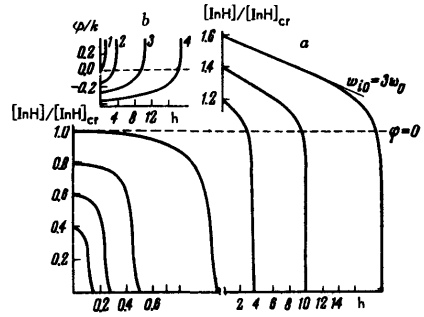


Fig. 5. *a*) Calculated kinetic curves for the consumption of inhibitor in the oxidation of a hydrocarbon with a ratio of the rate constant k_3 for dissociation of the hydroperoxide into radicals to the rate of generation of chains w_0 of $k_3/w_0 = 10^8$ litres mole^{-1}; *b*) variation in autocatalytic factor during reaction resulting from consumption of the inhibitor.

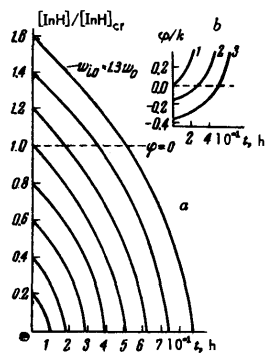


Fig. 6. *a*) Calculated kinetic curves for the consumption of inhibitor during the induction period in the oxidation of a hydrocarbon with a ratio of $k_3/w_0 = 10^5$ litres × × mole^{-1}; *b*) variation in autocatalytic factor during induction period resulting from consumption of inhibitor.

$[InH] < [InH]_{cr}$, but when $[InH] > [InH]_{cr}$ linear sections are present in which the inhibitor is consumed at a rate close to w_0. In this case the dependence of the induction period on the initial inhibitor concentration exhibits quite clear limiting phenomena (Fig. 4, curve *1′*). Autocatalytic consumption of the inhibitors 1- and 2-naphthols, 1- and 2-naphthylamines, and diphenylamine has been observed during the induction period in the oxidation of tetrahydronaphthalene (at 140°C),[27] cyclohexanone (at 120°C),[88] and hexadecane[89]. If the rate constant for dissociation of the intermediate product into radicals is small ($k_3 = 10^{-5}$ s^{-1}), the rate of initiation of chains due to degenerate branching may be close to the rate of generation of radicals. Fig. 6*a* shows that in this case the rate of consumption of inhibitor only slightly increases with time in comparison with the rate of generation of chains, and the induction period is proportional to the initial inhibitor concentration (Fig. 4, curve *3′*). A very frequent case is consumption of inhibitor at a constant rate, when the induction period is a

linear function of the inhibitor concentration. It follows from Figs. 6*a* and 4 that these regularities may be present at ratios of $k_3/w_0 \leq 10^5$ litres mole^{-1}. A constant rate of inhibitor consumption and a linear dependence of induction period on inhibitor concentration have been observed with the inhibitors *N*-phenyl-2-naphthylamine, 1-naphthol, and various alkylphenols in the oxidation of rubber[90], n-decane[87], ethyl methyl ketone, ethanol[91], and petrol[92].

Comparison of curves *1* and *1'*, *2* and *2'*, and *3* and *3'* in Fig. 4 shows that consumption of inhibitor diminishes the sharpness of the increase in induction period at the critical inhibitor concentration. It is seen from curves *1'* and *2'* that it is extremely difficult to determine $[InH]_{cr}$ when the transition through $\varphi = 0$ is unclear; extrapolation of the linear sections of the t_{ind}–$[InH]_0$ relationships yields values of $[InH]_{cr}$ which are too high.

However, the transition through $\varphi = 0$ should be sharp if $k_3/w_0 > 10^8$, and the experimental value of $[InH]_{cr}$ is close to the true value. The slope of the linear portions of curves *1'*–*3'* (Fig. 4) when $[InH] > [InH]_{cr}$ is close to the rate of generation of chains.

4. Results of Experimental Study of Critical Inhibitor Concentrations

Critical phenomena have been observed in the oxidation of n-decane in the presence of copper stearate as catalyst[93]. In this reaction the copper ions have a dual function, in that they catalyse the oxidation and act as inhibitor. The catalytic effect of copper stearate is already apparent at the very low concentrations of 10^{-5} mole % and right up to 0.060 mole %. At these concentrations the copper salt accelerates the formation of oxidation products — alcohols, ketones, and acids — in comparison with the uncatalysed reaction. At the same time the hydroperoxide concentration is diminished as compared with the uncatalysed reaction, more strongly the higher the copper stearate concentration. This fact indicates that the initiating effect of the copper salt is associated with an acceleration of the dissociation of hydroperoxide into radicals, as occurs with other metals of variable valency: $ROOH + Cu^{2+} \rightarrow RO_2\cdot$. Acceleration of the oxidation process, however, begins after a certain induction period has elapsed.

The plot of the variation in induction period with $CuSt_2$ concentration (Fig. 7) shows that the induction period gradually increases from 2 to 30 min up to $[CuSt_2] =$ = 0.06 mole %. Further slight increase in the copper stearate concentration by 0.005 mole % produces a sharp increase in the induction period of more than 15 h. Thus abrupt cessation of the reaction is observed at the critical copper stearate concentration of 0.065 mole %. This phenomenon may be associated with a transition at this concentration from autocatalytic ($\varphi > 0$) to steady-state ($\varphi < 0$) oxidation. The critical phenomenon in the presence of the copper salt is associated with the inhibiting action of copper ions.

The presence of a second, initiating action may explain the abrupt character of the transition to a steady state. The great rate of the catalysed dissociation of hydroperoxide into radicals ensures a rapid development of the reaction when $\varphi > 0$, and therefore the transition through the critical concentration $[CuSt_2]_{cr}$ occurs very sharply.

Critical phenomena are observed also in the oxidation of hydrocarbons in the presence of such typical inhibitors as phenols, naphthols, and amines. Figs. 8 and 9 show the dependence on inhibitor concentration of the induction period in the oxidation of ethylbenzene and n-decane in glacial acetic acid with cobalt acetate $CoAc_2$ as catalyst[40,87,94]. It is evident from these diagrams that a critical inhibitor concentration exists above which oxidation is sharply retarded, whereas induction periods are short at concentrations below $[InH]_{cr}$.

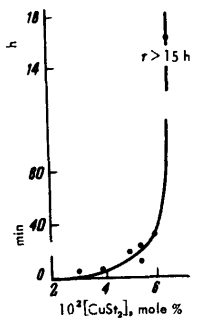


Fig. 7. Dependence of induction period in oxidation of n-decane on concentration of copper stearate at 140°C.

It has been shown[94] that the critical concentration of 1-naphthol varies little with temperature $E_{obs} = E_i - E_2 \simeq$ $\simeq$ 1 kcal mole^{-1}, is independent of the catalyst concentration (at $[CoAc_2] = 0.0056$–0.0565 M), and increases in proportion to the hydrocarbon concentration. These experimental results indicate that the effective activation energy and the dependence of the critical inhibitor concentration on the hydrocarbon concentration are consistent with Eqn. (23).

Table 3 lists experimental critical inhibitor concentrations together with values calculated from Eqn. (23) with

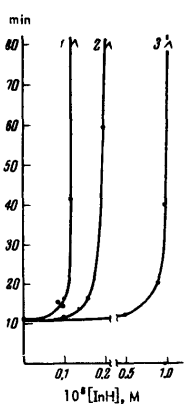


Fig. 8. Increase in induction period, in the oxidation of 2.6 M n-decane with 0.034 M cobalt acetate as catalyst in glacial acetic acid medium at 90°C, with increase in initial concentration of the inhibitors:
1) 1-naphthol; 2) tris-4-hydroxy-3,5-di-t-butylbenzylamine; 3) Ionol.

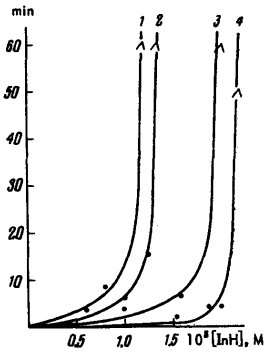


Fig. 9. Dependence of induction period, in the oxidation of ethylbenzene catalysed by 0.0113 M cobalt acetate at 60°C, on concentration of the inhibitors:
1) diphenylamine; 2) *N*-phenyl-2-naphthylamine; 3) 1-naphthol; 4) 2-naphthol.

TABLE 3. Comparison of experimental and calculated critical inhibitor concentrations in the catalysed oxidation of hydrocarbons.

Hydrocarbon	Inhibitor	$10^3[InH]_{cr}$, M		$\frac{[InH]_{calc}}{[InH]_{exp}}$
		expt.	calc.	
Ethylene-benzene*	Ionol	27.5	97	3.5
	1-naphthol	1.64	7.4	4.5
	N-phenyl-2-naphthylamine	1.3	10.5	8.1
	diphenylamine	1.0	8.9	8.9
	2-naphthol	1.8	34	19
n-Decane**	1-naphthol	0.2	0.56	3
	tris-4-hydroxy-3,5-di-t-butylbenzylamine	0.12	1.34	11
	Ionol	1.0	15	15

* From Ref. 94: [RH] = 3.24 M, $[CoAc_2]$ = 0.0113 M, [RH] : $[CH_3COOH]$ = 2 : 3, at 60°.

** From Ref. 40: [RH] = 2.6 M, $[CoAc_2]$ = 0.034 M, [RH] : $[CH_3COOH]$ = 1 : 1, at 90°C.

$n = 1$, $\delta = 1$, $m = 2$, and $\gamma = 1$. The ratio k_i/k_2 was determined by special methods in each case. The last column shows that the experimental values are lower than the calculated values. The discrepancy indicates that, at some stage in the oxidation or the breakdown of the hydroperoxide, new reactions, hitherto disregarded, appear in the system comprising the metal of variable valency and the inhibitor. Two hypotheses can be put forward to explain the increased effectiveness of antioxidants in the presence of cobalt ions.

In the calculation of the critical inhibitor concentration it was assumed that $\delta = 1$. However, the probability of degenerate branching may be less than unity, if the complex $[ROOH.CoAc_2]$ can react directly with the inhibitor to form valency-saturated compounds:

$$[ROOH \cdot Co(Ac)_2] + InH \rightarrow ROIn + Co(Ac)_2 + H_2O.$$

The second hypothesis is that the inhibitor may interact with the metal ion of higher valency to form an In radical:

$$(11)\quad Co^{3+}(Ac)_2(OH) + InH \rightarrow Co^{2+}(Ac)_2 + H_2O + In^{\cdot}.$$

The occurrence of this reaction in the mechanism of inhibited oxidation in the presence of metals of variable valency is highly probable. Phenoxy, naphthyloxy, and other radicals are formed in the reactions of phenols and naphthols with hydroperoxides in the presence of cobalt salts and of such compounds as PbO_2, $(CH_3COO)_4Pb$, and $K_3[Fe(CN)_6]$, which contain the metal in the higher valency state [58,73,95-97]. If the In· radicals react with the $RO_2^{\cdot}$ radicals, the occurrence of reaction (11) will increase the rate of chain termination.

It has been shown[40] that, when reaction (11) is taken into account, the critical inhibitor concentration is (with $\gamma = 1$)

$$[InH]_{cr} = \frac{k_2[RH]n\delta}{k_i}\sigma.$$

The parameter σ is defined by the formula

$$\frac{\sigma}{1-\sigma} = \frac{k_d[Co^{3+}][ROOH]}{k_{11}[Co^{2+}][InH]},$$

where k_d is the rate constant for the reaction of Co^{3+} with ROOH (see p. 267). If Co^{3+} reacts more rapidly with the hydroperoxide than with the inhibitor, $\sigma \rightarrow 1$. When $\sigma = 1$, the formula (23) is obtained for the critical inhibitor concentration. If, however, Co^{3+} reacts predominantly with the inhibitor, $\sigma < 1$, and the critical inhibitor concentration decreases.

Thus the formation of phenoxy-radicals in the reaction of Co^{3+} with an inhibitor should result in a lower critical inhibitor concentration, as is observed experimentally. The very abrupt cessation of oxidation at this critical concentration found in these experiments completely confirms the kinetic analysis of the transition through limiting conditions with degenerate chain branching. The rate constant for dissociation of the hydroperoxides of n-decane and ethylbenzene in the presence of cobalt acetate under these experimental conditions is of the order of $k_3 \simeq 10^{-2}\ s^{-1}$, while the rate of generation of chains is $w_0 \simeq 10^{-10}-10^{-11}\ M\,s^{-1}$. Thus the ratio $k_3/w_0 \geqslant 10^8-10^9$ litres $mole^{-1}$, which corresponds to the relationships *1* and *1'* in Fig. 4.

In all cases considered above, limiting phenomena were associated with change in the autocatalytic factor from positive to negative values in the initial stages of the reaction: i.e. the induction period depended on an external parameter, the inhibitor concentration. Cessation of an autocatalytic reaction which has already begun has been observed[98] when limiting conditions are reached during the process. The oxidation of n-decane was studied in the presence of potassium permanganate, which, just like copper stearate[93], has a dual role in the oxidation. Addition of 0.076–0.576 mole % of potassium permanganate halves the induction period in the oxidation of n-decane compared with autoxidation at the same temperature (140° C). The maximum concentration of peroxides in the presence of the permanganate is one-third of that in the uncatalysed reaction, owing to participation of the catalyst in its radical dissociation.

Potassium permanganate was found to have an inhibiting as well as an initiating and controlling function. Fig. 10 shows kinetic curves for the accumulation of acids at various permanganate concentrations. It is seen that a reaction which has developed is abruptly stopped at different degrees of conversion depending on the permanganate concentration. The limiting yield of acids decreases with increase in this concentration.

Separate experiments in which potassium permanganate was withdrawn showed that the cessation of the reaction is due to chain termination involving a manganese salt. It

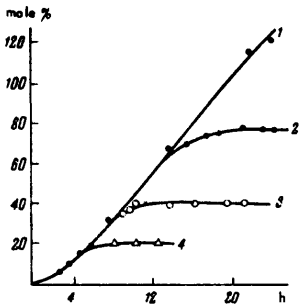


Fig. 10. Kinetic curves for the accumulation of acids in the presence of potassium permanganate (mole %):
1) 0.768; 2) 0.192; 3) 0.384; 4) 0.576.

follows from Eqn. (23) that the limiting condition can be reached if the hydrocarbon is exhausted to a definite concentration $[RH]_{cr}$. Fig. 11 shows that the hydrocarbon concentration at which reaction ceases is a linear function of the potassium permanganate concentration. This supports the conclusion that the cessation of oxidation in the presence of potassium permanganate is associated with the achievement of a limiting condition.

A critical solvent (benzene) concentration has been observed[99] in the oxidation of liquefied butane dissolved in it at temperatures and pressures close to the critical values (170°C and 50 atm). A certain relationship was observed to exist between the concentrations of butane and benzene

$$\gamma_{cr} = \frac{[RH]}{[C_6H_6] + [RH]},$$

below which butane is not oxidised at all, and above which the usual autocatalytic reaction develops.

Fig. 12*a* shows that the yield of acetic acid falls as the proportion of benzene in the initial mixture is increased, until a value corresponding to $\gamma = 0.28$ is reached, at which reaction ceases completely. This phenomenon can be seen in Fig. 12*b*, which illustrates the dependence on γ of the quantity of acetic acid formed during 2 h of the reaction. When mixtures having $\gamma > 0.28$ are taken for an experiment, reaction continues until the value $\gamma_{cr} = 0.28$ is reached (Fig. 12*c*).

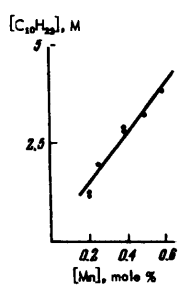


Fig. 11. Dependence of limiting hydrocarbon concentration on initial concentration of potassium permanganate.

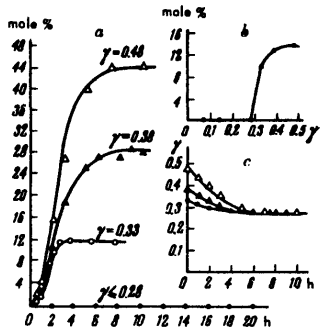


Fig. 12. *a*) Kinetic curves for the accumulation of acetic acid in the oxidation of liquefied butane in benzene at 170°C and 50 atm with various initial ratios γ of butane to benzene; *b*) dependence on γ of quantity of acetic acid formed in 2 h of reaction at 170°C and 50 atm; *c*) variation in γ during reaction.

It is assumed that in this reaction $RO_2^{\cdot}$ radicals add on to the benzene molecule, with the formation of relatively inactive radicals, which are incapable of chain propagation.

V. PHENOMENON OF A CRITICAL INHIBITOR CONCENTRATION IN THE CONTINUOUS OXIDATION OF HYDROCARBONS IN REACTION VESSELS WITH IDEAL MIXING (OPEN SYSTEMS)

All the experimental results discussed above on critical phenomena in the inhibited oxidation of hydrocarbons, and the kinetic analysis of this phenomenon, have related to batch processes occurring in a closed system. In such processes the starting materials are introduced into the reaction vessel in a single step at the start of the reaction, and remain together with the reaction products inside the reaction vessel until the end of the process. However, experimental results[14,100,101] show that the existence of limiting conditions in the inhibited oxidation of hydrocarbons is exhibited most clearly when the process is conducted continuously in reaction vessels with ideal mixing. In this method of conducting a process the starting materials enter continuously, at a rate u (in ml h^{-1}), a reaction vessel of volume V (ml), while a proportion of the reaction products are removed from the vessel at the same rate. Vigorous stirring should ensure a uniform concentration of the reaction components throughout the vessel. Such unclosed systems, which represent a flow system with perfect mixing, have been termed open systems, since every volume element is "open" for the entry of new substances[102].

The variation in concentration of the reactants in a continuous process can in general be represented by the equation

$$\frac{d[A_i]}{dt} = w_f - w_r + v[A_i]_0 - v[A_i].$$

where w_f and w_r are the rates of formation and removal of a component A_i by chemical reactions. The product $v[A_i]_0$ represents the rate of increase in concentration of this component resulting from its entry into the reaction vessel as a solution of concentration $[A_i]_0$; and the term

$-v[A_i]$ allows for the decrease in concentration of the component A_i due to the withdrawl of reaction products. The parameter v is the ratio $v = u/V$. When a process is conducted in this way, the concentration of each component A_i ceases to vary ($d[A_i]/dt = 0$) after a certain time, because the sum of the rates at which the concentration of the substance increases ($w_f + v[A_i]_0$) becomes equal to the sum of the rates at which the concentration decreases ($w_r + v[A_i]$).

In the steady state ($d[A_i]/dt = 0$) the rates w_f and w_r are constant, and the concentrations of the reactants remain unchanged indefinitely. The establishment of a steady-state chemical reaction in an open system is its most important feature [103-107].

In several cases of complex chemical reactions, the possibility has been shown both theoretically and experimentally of harmonic oscillations about the steady state [108-111].

In several cases the study of simple and complicated reactions under steady-state conditions, with the reaction conducted as a continuous process, permits the solution of many problems associated with the mechanism of the reaction. In particular, it is possible in open systems to study unstable intermediate products [103]. A new method has been proposed [112,113] for investigating, in complicated chain oxidations of hydrocarbons, the reactivities of various substances towards $RO_2^{\cdot}$ radicals, and for measuring the rates of formation and of consumption of the reaction products, etc.

The oxidation of a hydrocarbon has been studied [100,101] in the presence of an inhibitor in an open system. Fig. 13 illustrates the accumulation of hydroperoxide in the oxidation of n-decane in the presence of 1-naphthol as inhibitor. A reaction vessel of volume $V = 5$ ml was filled with n-decane containing 1-naphthol in concentrations which varied from experiment to experiment, and from the start of oxidation a similar solution was automatically and continuously fed into the vessel at a rate of $u = 2.6$ ml h^{-1}. Oxygen was bubbled through the oxidising hydrocarbon at 1.6 litres h^{-1}, and at the same time stirred the mixture. Fig. 13 shows that, with a continuous supply of pure n-decane in the absence of inhibitor (curve *1*) the concentration of the reaction product (hydroperoxide) increases to a certain value (0.8 mole %), after which the reaction proceeds at a constant rate.

If n-decane containing 1-naphthol enters the reaction vessel, increase in the inhibitor concentration over the range $(3-9) \times 10^{-6}$ M is accompanied by a lengthening of the induction period, but the previous steady state is established after the end of the induction period.

With further slight increase in the inhibitor concentration from 9×10^{-6} to 9.05×10^{-6} M a sudden change in the rate of the process occurs: the reaction does not emerge from the induction period, and oxidation does not take place. The critical character of the dependence of the induction period of the reaction and the hydroperoxide concentration in the steady state on the initial inhibitor concentration is evident from Fig. 13*b*.

Similar critical phenomena in the oxidation of n-decane in an open system have been observed with tris-4-hydroxy-3,5-di-t-butylbenzylamine as inhibitor (Fig. 14).

The relation between the phenomenon of a critical inhibitor concentration in a continuous process and the mechanism of oxidation has been analysed [94]. The variation in concentration of radicals r (= $RO_2^{\cdot}$), hydroperoxide x (ROOH), inhibitor i (InH), and hydrocarbon [RH] in an open system is described by the equations

$$dr/dt = w_0 + nk_3x - mk_i ir - k_6 r^2 = 0, \quad (25)$$

$$dx/dt = k_2[RH]r - (k_3 + k_3' + v)x, \quad (26)$$

$$di/dt = -k_i ir - vi + vi_0, \quad (27)$$

$$d[RH]/dt = -k_2 r[RH] - v[RH] + v[RH]_0. \quad (28)$$

In the experiments illustrated in Figs. 13 and 14, hydrocarbon and inhibitor enter the reaction vessel continuously at rates of $v[RH]_0$ and vi_0 respectively, and hydrocarbon, inhibitor, and hydroperoxide and other reaction products leave the reaction vessel continuously at rates of $-v[RH]$, $-vi$, and $-vx$ respectively, where [RH], i, and x are the concentrations of the corresponding substances in the reaction vessel. The change in concentration of radicals due to withdrawal of oxidation product ($-vr$) is insignificant, and can be neglected. In the equation for dx/dt the formation of hydroperoxide in chain termination on the inhibitor is disregarded, which is valid with sufficiently long chains ($\nu > 1$). With long chains the parameter γ, which determines the participation of RO and OH radicals in chain

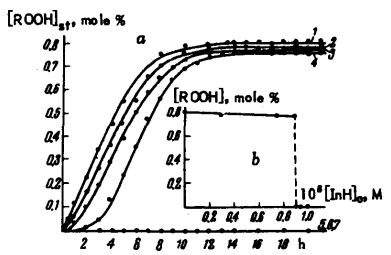


Fig. 13. *a*) Kinetic curves for the accumulation of hydroperoxide in the continuous oxidation of n-decane in the presence of 1-naphthol (M): 1) 0; 2) 3×10^{-6}; 3) 7.5×10^{-6}; 4) 9.00×10^{-6}; 5) 9.05×10^{-6}; 6) 1.2×10^{-5}; 7) 1.4×10^{-5}. *b*) Dependence of steady-state concentration of hydroperoxide on initial concentration of 1-naphthol.

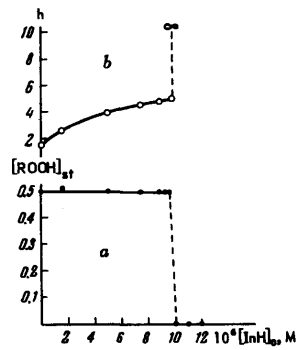


Fig. 14. Dependence, on concentration of tris-4-hydroxy-3,5-di-t-butylbenzylamine with inhibitor solution entering reaction vessel at a rate of $v = 1.83 \times 10^{-4}$ s^{-1} at 130°C, of: *a*) steady-state concentration of n-decane hydroperoxide; *b*) induction period.

propagation, is close to unity, and reactions of these radicals with the inhibitor can be disregarded. It is assumed that the In radicals are involved only in chain termination.

Provided that $k_5 r^2 \ll m k_i r i$, the equations for dr/dt and dx/dt can be combined to give

$$dx/dt = \nu w_0 + \varphi x,$$

where $\nu = k_2[RH]/mk_i i$ is the chain length, $\varphi = k_3(\nu - 1/\delta)$ the autocatalytic factor, and $\delta = k_3/(k_3 + k_3' + v)$ the probability of degenerate chain branching in the continuous process.

A feature of continuous reactions with perfect mixing of the components of the reaction mixture is the establishment of steady-state concentrations of the starting materials $[RH]_{st}$ and i_{st} and of the reaction products x_{st}, when the process occurs at a constant rate, so that $dx/dt = 0$, $di/dt = 0$, and $d[RH]/dt = 0$:

$$\nu w_0 + \varphi x_{st} = 0, \quad (26')$$

$$-k_i i_{st} r_{st} - v i_{st} + v i_0 = 0, \quad (27')$$

$$-k_2 r_{st}[RH]_{st} - v[RH]_{st} + v[RH]_0 = 0.$$

It follows from Eqn. (26') that, under steady-state conditions of continuous oxidation with chain termination on an inhibitor, the autocatalytic factor should always be negative ($\varphi < 0$), since both νw_0 and x are positive. The inhibitor concentration in the steady-state i_{st} should therefore exceed the value $i_{\varphi=0}$ at which the autocatalytic factor is zero:

$$i_{st} > i_{\varphi=0} = \frac{k_2[RH]n\delta}{mk_i}. \quad (29)$$

Let us denote the steady state established during oxidation in the presence of an inhibitor as state (I). In this state the rate of reaction of the hydrocarbon is very small. It follows from Eqn. (26') that the hydroperoxide concentration x_{st} at $\varphi < 0$ is given by

$$x_{st} = \frac{\nu w_0}{|\varphi|} = \frac{w_0}{nk_3(i_{st}/i_{\varphi=0} - 1)}.$$

When $i_{st}/i_{\varphi=0} = 1.4$, for example, the concentration of the intermediate product is $x_{st} = 1.1 w_0/k_3$ (with $n = 2$), and right up to the value $w_0/k_3 = 5 \times 10^{-4}$ M it is impossible to detect hydroperoxide in the steady state (I) by the usual iodometric method.

If the concentration of inhibitor falls to $i_{\varphi=0}$ during the oxidation, the autocatalytic factor of the process becomes zero.

Eqn. (26') shows that, when $\varphi \geq 0$, the reaction cannot arrive at the steady state (I). When $\varphi > 0$, the reaction is autocatalytic, the concentration of radicals r increases, and inhibitor is consumed. A new steady state (II) is then established, associated with high rates of autocatalytic oxidation.

The oxidation of a hydrocarbon in the presence of an inhibitor in an open system has been simulated by the numerical integration of Eqns. (25)–(28) on an electronic computer. The parameters and elementary rate constants, obtained experimentally under conditions of the liquid-phase autoxidation of the hydrocarbons, chosen for the simulation were $w_0 = 10^{-10}$ M s^{-1}, $[RH] = 5.0$ M, $k_2 = 2.0$ litres mole^{-1} s^{-1}, $k_i = 2 \times 10^5$ litres mole^{-1} s^{-1}, $k_5 = 2 \times 10^7$ litres mole^{-1} s^{-1}, $k_3 = 10^{-4}$ s^{-1}, $k_3' = 0$, $v = 1.7 \times 10^4$ s^{-1}, $m = 1$, and $n = 1$.

Fig. 15 gives the calculated kinetic curves for the accumulation of intermediate product, and also the change in its concentration in the steady state and the induction period with different inhibitor concentrations. It is seen from Figs. 13–15 that the calculated relationships completely reproduce the rules observed experimentally.

Fig. 16 shows the variation in the autocatalytic factor of the process at inhibitor concentrations $[i_0]$ of $0.96[i_0]_{cr}$ (curve *2*) and $1.04[i_0]_{cr}$ (curve *1*). At an inhibitor concentration slightly exceeding the critical value, the autocatalytic factor remains negative until the steady state is established. At this innibitor concentration the rate of oxidation of the hydrocarbon is insignificant (Fig. 15*a*). At an inhibitor concentration below the critical value the autocatalytic factor is at first negative, passes through zero, and then assumes positive values. In this case the reaction is autocatalytic (Fig. 15, curve *3*).

Thus the critical phenomena in an open system represent a transition from a steady-state process ($\varphi < 0$) to an autocatalytic process ($\varphi > 0$), as occurs in a closed system.

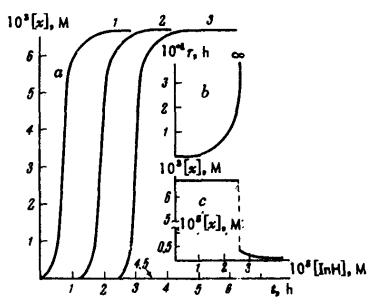


Fig. 15. *a*) Calculated kinetic curves for the accumulation of hydroperoxide in the continuous oxidation of a hydrocarbon in the presence of an inhibitor at an initial concentration $[i_0]/[i_0]_{cr}$ of: 1) 0; 2) 0.8; 3) 0.96; 4) 1.04; 5) 1.2.
b) Variation in induction period in presence of inhibitor with continuous oxidation.
c) Dependence of steady-state concentration of hydroperoxide on concentration of inhibitor.

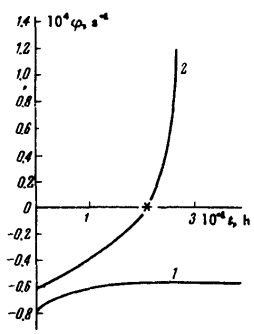


Fig. 16. Variation in autocatalytic factor during continuous oxidation of a hydrocarbon at inhibitor concentrations $[i_0]/[i_0]_{cr}$ of: 1) 1.04; 2) 0.96.

However, limiting conditions of oxidation are very sharply developed in an open system, and well-defined critical phenomena are observed even under conditions under which, in closed systems, the transition through $\varphi = 0$ is not accompanied by an abrupt change in the rate of the process (Fig. 4, curve *3*). The reason for this will become clear from a comparison of Fig. 16 with Figs. 5*b* and 6*b*, which illustrate the variation in the autocatalytic factor in continuous and batch processes.

In a batch process the inhibitor is introduced into the oxidising hydrocarbon in a single step, at the start of the reaction, and is continuously consumed during the reaction. The time of the steady-state development of the reaction (when $\varphi < 0$) in a closed system is limited by the time for the inhibitor to be exhausted to the critical concentration, and at any initial inhibitor concentration exceeding the critical value a transition will occur from the steady-state to the autocatalytic process ($\varphi > 0$) when the inhibitor has been consumed to the critical concentration.

In an open system the reaction cannot emerge from the steady state ($\varphi < 0$) for an infinite time. The advantage of an open system in revealing the limiting conditions of a process was emphasised[114] in connection with an analysis of the conditions of ignition in an exothermic reaction occurring in an adiabatic flow system with perfect mixing: "The boundary between spontaneous ignition and a steady state is absolutely sharp; physically this is connected with the fact that, in a flow system with a continuous supply of material, we can leave the system for an indefinite... time to reveal whether or not a steady state has been reached".

It has been shown theoretically[115] that several steady states may exist in an open system in which a composite process is occurring, consisting of a set of unimolecular and bimolecular reactions among N components. In particular, two stable steady states should occur in oxidation with a continuous supply of inhibitor together with the initial hydrocarbon to the reaction vessel.

The critical inhibitor concentration in an open system can be evaluated from Eqns. (26′) and (27′). These equations can be combined to give

$$x_{st}^2 - x_{st}\left[\frac{(mvi_0 - w_0)}{nk_3} - \frac{vk_2[RH]_{st}}{kk_i}\right] + \frac{vw_0k_2[RH]_{st}}{nk_3kk_i} = 0.$$

When $[i_0] > [i_0]_{cr}$, this equation has two positive roots, the smaller of which corresponds to the steady state (I), while the larger root defines an unstable state. When $[i_0] = [i_0]_{cr}$, the two roots are equal; and when $[i_0] < [i_0]_{cr}$, the equation has no positive root. Thus the value of $[i_0]_{cr}$ is determined from the condition that the above equation should have equal roots:

$$[i_0]_{cr} = (\sqrt{i_{\varphi=0}} + \sqrt{w_0/mv})^2. \qquad (30)$$

From the critical inhibitor concentration $[i_0]_{cr}$ we can determine by means of Eqns. (29) and (30) the relative activities k_i/k_2 of inhibitors towards chain radicals. For the inhibitors 1-naphthol and tris-4-hydroxy-3,5-di-t-butylbenzylamine the values of this ratio determined from experimental data (Figs. 13 and 14) were 3.8×10^5 and 6.5×10^4 respectively, which are very close to the values of 5.8×10^5 and 8.5×10^4 obtained by an independent method from experiments on the initiated oxidation of n-decane and by a chemiluminescent method[70].

Thus the striking property of branched chain processes — the existence of critical (limiting) phenomena — is clearly revealed in a variety of ways even with slow non-stationary processes with degenerate chain branching. Clear critical effects occur in the oxidation of organic compounds, especially in the condensed state (liquid phase). The presence of these effects, which confirms so vividly the branched chain character of the corresponding processes, should undoubtedly be taken into account in developing a general theory of the action of inhibitors (antioxidants), and will play its part in working out optimum conditions for the practical use of inhibitors, e.g. for the suppression of undesirable oxidative changes.

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PRESENT STATE OF THE THEORY OF THERMAL EXPLOSIONS

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I. INTRODUCTION

Studies of scientific and practical problems associated with thermal explosions have attracted considerable interest in recent years. These investigations are highly relevant not only to the development of the physics of combustion and of explosions, which includes the theory of thermal explosions as one of its subdivisions, but also to fundamental branches of knowledge such as chemical kinetics and the theory of heat transfer. The phenomenon of thermal explosion is used in the laboratory as a method of physicochemical research. Thermal explosion is the simplest among the forms of transformation of matter considered in the physics of combustion and of explosion. Therefore the formalism of the theory of thermal explosions finds application in the study of more complicated phenomena, such as the initiation of explosion by external (non-thermal) effects (impact, friction, etc.), multistage combustion, and detonation. The practical interest in thermal explosion processes arises mainly from problems of industrial safety in some types of operation with explosive systems (processing, manufacture of articles, explosive operations in high-temperature boreholes, etc.). In many cases, safe conditions excluding the possibility of spontaneous explosion can in principle be predicted, on the basis of the theory of thermal explosions.

The first quantitative formulation of the theory of thermal explosions was published in 1928 by Semenov [1], who used the simplest ideas on the evolution and extraction of heat to calculate critical conditions leading to thermal explosion, and the heating effect preceding explosion. This paper by Semenov laid the foundations for the development of the theory of thermal explosions, and stimulated numerous investigations in the 1930's, notably those of Todes, Rice, Frank-Kamenetskii and others [2-10]. A generalised treatment of these researches, which we shall call the classical theory of thermal explosions, was given in a review by Semenov [11] and in monographs by Frank-Kamenetskii [12] and by Semenov [13].

Since gas-phase reactions were studied intensively in the investigation of chemical kinetics in the 1930's, the classical theory of thermal explosion deals mainly with gases. In later years, in connection with the great interest taken in condensed matter, systematic studies of thermal explosions in condensed media were begun. These studies contributed to the development of the general principles of the theory as well as to some specific aspects characteristic of condensed phases.

No reviews dealing with the work done since the formulation of the classical theory of thermal explosions have appeared in the literature. A few papers have been discussed [14] from the standpoint of the thermophysical aspects of the theory of thermal explosions. Thus the present review is of definite interest, since it gives an account of the present state of the theory of thermal explosions and suggests probable lines along which further development can be expected.

II. GENERALISATION AND DEVELOPMENT OF THE CLASSICAL THEORY OF THERMAL EXPLOSIONS

In the classical theory, the problem of thermal explosion is formulated as follows: given a region (or vessel) containing the reactant, knowing the kinetic laws of the evolution of heat and the mechanism of heat transfer within the region, and given the initial and boundary conditions, we are required to determine the basic parameters of the phenomenon (the critical conditions and the induction period). The actual expressions for the evolution and extraction of heat used in the classical theory are based on the simplest model of these phenomena, applicable to gaseous systems.

Generalising and making more concrete some initial premises adopted by Semenov, Frank-Kamenetskii, and

Todes, we shall formulate the essential outlines of the classical model in the following way:

1. The reaction taking place in the region under study occurs in one stage and is irreversible.

2. Heat transfer in the reaction zone occurs by conduction. There is no motion of the reacting substance, and therefore no convective heat transfer.

3. The starting material and the reaction products are in the same state of aggregation, i.e. the reaction is not accompanied by any phase transition.

4. The boundary of the region is impermeable to matter. Heat exchange at the boundary obeys Newton's law.

5. The physical parameters of the material (thermal conductivity, specific heat, density), the characteristics of the chemical reaction (activation energy, pre-exponential factor, enthalpy), and the conditions under which the reaction proceeds (pressure, temperature of the surrounding medium, shape and size of the region, emissivity) remain constant throughout the reaction.

This model, the simplest possible, has been widely applied to the study of thermal explosions in condensed as well as in gaseous media.

A mathematical statement of the problem, which satisfies the above premises, leads to the familiar equations of the classical theory

$$c\rho\frac{\partial T}{\partial t} = Q\frac{\partial \eta}{\partial t} + \lambda\left(\frac{\partial^2 T}{\partial x^2} + \frac{n}{x}\frac{\partial T}{\partial x}\right),$$

$$\frac{\partial \eta}{\partial t} = k_0 e^{-\frac{E}{RT}}\varphi(\eta).$$

Boundary conditions:

$$x = 0, \frac{\partial T}{\partial x} = 0;\ x = r, -\lambda\frac{\partial T}{\partial x} = \alpha(T - T_0).$$

Initial conditions:

$$t = 0,\ T = T_{init},\ \eta = 0.$$

We shall deal with symmetrical regions, of plane-parallel ($n = 0$), cylindrical ($n = 1$), and spherical geometry ($n = 2$).

Symbols. The following symbols will be adopted:

T temperature in the reaction zone (°K);
T_0 temperature of the surrounding medium (°K);
T_{init} initial temperature of the substance (°K);
η extent of reaction;
x spatial coordinate (cm);
r the characteristic dimension of the region (radius of the vessel)(cm);
t time (s);
Q the exothermicity of the reaction (cal cm^{-3});
E activation energy (cal mole^{-1});
k_0 pre-exponential factor (s^{-1});
λ thermal conductivity of the material (cal cm^{-1} × × s^{-1} deg^{-1});
c specific heat (cal g^{-1} deg^{-1});
ρ density (g cm^{-3});
α thermal emissivity coefficient (cal cm^{-2} s^{-1} deg^{-1}).

The function $\varphi(\eta)$ expresses the law governing the reaction under isothermal conditions:

$\varphi(\eta) \equiv 1$ for a zero-order reaction;
$\varphi(\eta) = (1 - \eta)^m$ for a reaction of order m;
$\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$ for a first-order autocatalytic reaction;
η_0 the criterion for autocatalysis (ratio of initial reaction rate to autocatalytic constant).

This system of equations, when reduced to dimensionless quantities as suggested by Frank-Kamenetskii, takes the form

$$\frac{\partial\theta}{\partial\tau} = \varphi(\eta)\exp\frac{\theta}{1+\beta\theta} + \frac{1}{\delta}\left(\frac{\partial^2\theta}{\partial\xi^2} + \frac{n}{\xi}\frac{\partial\theta}{\partial\xi}\right);\ \frac{\partial\eta}{\partial\tau} = \gamma\varphi(\eta)\exp\frac{\theta}{1+\beta\theta}. \quad (1)$$

Boundary conditions:

$$\xi = 0, \frac{\partial\theta}{\partial\xi} = 0;\ \xi = 1, \frac{\partial\theta}{\partial\xi} = -\mathrm{Bi}\cdot\theta.$$

Initial conditions:

$$\tau = 0, \theta = -\theta_{init}, \eta = 0.$$

Dimensionless variables:

$$\theta = \frac{E}{RT_0^2}(T - T_0) \text{ initial heating up},$$

$$\xi = \frac{x}{r} \text{ coordinate},$$

$$\tau = t\cdot\frac{Q}{c\rho}\frac{E}{RT_0^2}k_0\exp\left(-\frac{E}{RT_0}\right) \text{ time}.$$

Dimensionless parameters:

$$\delta = \frac{Q}{\lambda}\frac{E}{RT_0^2}r^2k_0\exp\left(-\frac{E}{RT_0}\right),$$

is the Frank-Kamenetskii criterion, giving the relationship between the scale factors for the supply and the dissipation of heat (the fundamental parameter in the theory of thermal explosions).

$\mathrm{Bi} = \alpha r/\lambda$ is the familiar Biot criterion of the theory of heat transfer, which characterises the relationship between external and internal heat transfer. The case of $\mathrm{Bi} \to \infty$ corresponds to constant surface temperature, whereas $\mathrm{Bi} \to 0$ denotes absence of temperature gradients in the vessel under consideration.

$$\theta_{init} = \frac{E}{RT_0^2}(T_0 - T_{init}),$$

is the initial temperature excess of the surroundings, which determines the role of the heating-up stage, and

$$\beta = \frac{RT_0}{E} \text{ and } \gamma = \frac{c\rho}{Q}\frac{RT_0^2}{E},$$

are parameters which characterise the "quality" of the thermal explosion as a limiting case of reaction under non-isothermal conditions. For normal, non-degenerate régimes, $\beta \ll 1$ and $\gamma \ll 1$, and the theory of thermal explosions usually deals with the limiting cases $\beta \to 0$ and $\gamma \to 0$.

Solution of the general system of equations (1) presents great mathematical difficulties. Therefore approximate ways of approaching the problem — known as the stationary and the non-stationary theory of thermal explosions — have been developed within the classical theory. Table 1 lists some concrete examples of solutions of the equations for thermal explosions, discussed in the classical theory

TABLE 1.

Cases considered						Type of solution*	Method**	Ref.
θ_{init}	n	Bi	β	γ	$\varphi(\eta)$			
—	—	→0	β	—	1	s	a	1
—	—	0	β	τ	1—η; (1—η)²	n	a	2
$\theta_{init} \leq 0$	—	→0	β	τ	1 ; 1—η (η+η₀)(1—η)	n	n	4,5
—	0	∞	0	—	1	s	a	
—	1; 2	∞	0	—	1	s	n	9
0	—	→0	0	τ	$(1-\eta)^m$	n	a	
—	1; 2	∞	0	—	1	s	a	25
—	0; 1	Bi	0	—	1	s	a	29,30
—	2	Bi	0	—	1	s	n	
—	0; 1; 2	∞	β	—	1	s	n	36
0	—	→0	—	—	1	n	a	32
0	—	→0	—	τ	$(1-\eta)^m$	n	a	38
0	0; 1; 2	Bi	β	τ	1 ; 1—η; (η+η₀)(1—η)	n	n	42,45
0	—	→0	0	—	(η+η₀)(1—η)	q	a	44
0	1	∞	0	—	(η+η₀)(1—η)	q	a	46
$\theta_{init} > 0$	0; 1; 2	∞	β	—	1	n	n	15
$\theta_{init} > 0$	0; 1; 2	Bi	β	τ	1 ; 1—η; (η+η₀)(1—η)	n	n	16—19

* s = stationary; n = non-stationary; q = quasistationary.
** a = analytic; n = numerical integration.

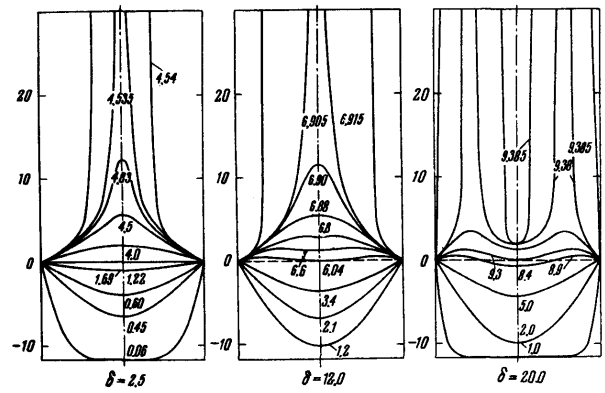

Fig. 1. Non-stationary temperature profiles during ignition with allowance for the heating-up stage [16]:
$n = 1$; $\theta_{init} = 11.7$; $\beta = 0.03$; $\gamma \to 0$. The numbers on the curves give the values of τ.

and also in more recent work. It is evident that generalisation and development of the classical theory have proceeded by making due allowance for the heating-up stage, considering the various modes of heat transfer at the surface, and elucidating the role of isothermal self-acceleration of the reaction (autocatalysis). Also, various approximate procedures have been developed within the framework of the stationary and the non-stationary theories.

We shall now briefly consider the main results of papers devoted to the generalisation and development of the classical theory.

1. Thermal Explosion as an Ignition Régime

Usually, a substance has to be heated to some definite temperature in order to achieve thermal explosion. The classical theory considers that the heating-up stage is unimportant and can be ignored.

Zinn and Mader [15] were the first to solve the thermal explosion equation with allowance for the heating-up stage, by numerical integration on an electronic computer for the case of a zero-order reaction, but they gave no general conclusions (either qualitative or quantitative). Abramov, Gontkovskaya, and one of us made some more detailed calculations [16-19], which revealed the specific effects which arise with a heating-up stage and explained the place of thermal explosions within the more general framework of ignition régimes. They also formulated the conditions under which conventional views on the role of the heating-up stage can be applied to thermal explosions.

The main conclusions of these investigations are based on an analysis of temperature distribution curves in space and time. (The most typical cases are illustrated in Fig. 1). Ignition in the presence of a heating-up stage proceeds in the following way.

In general, the heating-up of the system as a result of an exothermic reaction does not occur simultaneously throughout the volume. A temperature of T_0 is reached initially in the surface layers, and spreads to the inner layers. Temperature maxima appear close to the surface, and in time these grow and move towards the centre: in other words, a heat-evolution wave of increasing amplitude moves from the surface towards the centre of the vessel. The magnitude of the heating effect at the maximum increases faster than linearly with time, leading to ignition, which may occur either at the centre (when the heating-up wave reaches the centre, and the maxima coalesce) or at some distace from it.

This state of affairs is very sensitive to the parameter δ. At low values of δ this model degenerates, and heating-up proceeds practically simultaneously at all points in the reaction volume, so that there are no heating-up waves. As δ increases, the wave character of the heating-up stage becomes more and more distinct, and for very large values of δ the system does not heat up: ignition occurs when the central regions of the material are almost at the initial temperature.

The change in ignition régime as δ increases is conveniently observed from the change in position of the point corresponding to the onset of ignition, whose coordinate we shall denote $\xi_{expl}(\delta)$ (see Fig. 2). The plot of ξ_{expl} against δ shows two critical values of δ: (*a*) δ_{cr}, the lower limit of thermal explosion, is the value of δ which separates the ignition region from the region of non-explosive reaction (this quantity is known from the classical theory, and its value has been calculated by Frank-Kamenetskii); (*b*) δ'_{cr}, the upper limit of thermal explosion, is a value which separates two ignition régimes according to whether

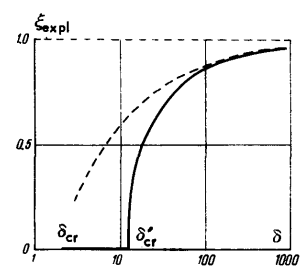

Fig. 2. Variation of ξ_{expl} with δ for the same values of the parameters as in Fig. 1. The broken line gives the limiting curve for ignition [16].

ignition sets in at the centre of not. This is essentially a new characteristic of thermal explosions, revealed by a consideration of the heating-up process — allowance for the parameter θ_{init} in the initial conditions of the system of equations (1) — and was not recognised until recently

Thus, according to the value of δ, we can distinguish the following régimes —

$\delta \ll \delta_{cr}$ the reaction proceeds isothermally (with very fast initial heating)
$\delta < \delta_{cr}$ the reaction proceeds non-isothermally, but non-explosively (with rapid heating-up and a heat-evolution stage)
$\delta_{cr} < \delta < \delta'_{cr}$ thermal explosion (self-ignition)
$\delta > \delta'_{cr}$ transition from thermal explosion to ignition
$\delta \gg \delta'_{cr}$ ignition.

We shall stress two important conclusions relating to this problem.

(*a*) Under the most favourable conditions (constant surface temperature and absence of isothermal autocatalysis) the region of thermal explosions is very narrow. It has been found[17] that the ratio δ'_{cr}/δ_{cr} is ~ 10 for a flat layer, ~ 6 for an infinite cylinder, and ~ 4 for a sphere. This corresponds to a range of about 1–2 critical diameters or a few tens of degrees. Decrease in the coefficient of heat transfer from the surface to the surrounding medium[18] and the appearance of isothermal autocatalysis[19] lead to a wider region of thermal explosion. When $Bi \to 0$, $\delta'_{cr} \to \infty$: obviously, if the system does not contain temperature gradients, ignition can occur only under the thermal explosion régime.

(*b*) Over the whole range $\delta_{cr} < \delta < \delta'_{cr}$ the overall time lag of the ignition τ_{expl} can be separated into a heating-up time τ_{heat} and an induction period τ_{ind}:

$$\tau_{expl} = \tau_{heat} + \tau_{ind},$$

the quantity τ_{ind} being almost independent of θ_{init}, i.e. of whether or not a heating-up stage is present. This separation was found to be possible even when $\tau_{heat} > \tau_{ind}$.

Thus, the framework of classical theory, which assumes $T_{init} = T_0$ ($\theta_{init} = 0$), can also be used when a heating-up stage is present, but only over a certain range of values of δ.

It is interesting to note that the formulation of the problem of thermal explosions with allowance for the heating-up stage is essentially equivalent to a general formulation of the problem in the theory of combustion, and that the equations considered in the thermal theory of ignition[20–23] for a semi-infinite space represent a limiting case of the system of equations (1) when $\delta \to \infty$. An analysis of the phenomenon close to the limiting region $\delta \to \infty$ has been made by Zel'dovich[24]. Problems in the general theory of combustion are being intensively studied at the moment by numerical integration of Eqns. (1) with the help of an electronic computer. This approach has revealed the main features of the phenomenon, and has enabled some quantitative generalisations to be made, but we still lack an approximate mathematical theory for the transition region (and in particular for calculating the value of δ'_{cr}).

2. Steady-State Theory of Thermal Explosions

The steady-state theory of thermal explosions is an approximate method for calculating the critical conditions (the δ_{cr} values) and the temperature distributions. It consists in solving the equation

$$\frac{d^2\theta}{d\xi^2} + \frac{n}{\xi}\frac{d\theta}{d\xi} = -\delta \exp\frac{\theta}{1+\beta\theta}, \qquad (2)$$

with the boundary conditions

$$\xi = 0.\ \frac{d\theta}{d\xi} = 0;\ \xi = 1.\ \frac{d\theta}{d\xi} = -\mathrm{Bi}\cdot\theta.$$

Explosion is treated as the absence of a solution for the steady-state equation (2). The approximation arises mainly from neglect of the combustion of material which occurs during the induction period: in other words, the reaction is assumed to be of zero order.

In the classical theory, Eqn. (2) is solved in two limiting cases —

$Bi \to 0$, β arbitrary (Semenov's theory)
$Bi \to \infty$, $\beta \to 0$ (Frank-Kamenetskii's theory)

The steady-state theory has been developed further in recent years[25–31]. The most interesting achievement is the generalisation of the classical theory[29,30] for the case of an arbitrary value of the Bi parameter, which is particularly relevant to the discussion of thermal explosions in condensed media. The régime $Bi \to \infty$ (constant temperature of the walls of the vessel) usually applies to gases; condensed phases, on the other hand, can have any value of Bi, including both limiting cases and the transition region. The variation of δ_{cr} with Bi for $\beta = 0$ has been obtained in the form of a transcendental equation for the case of planar geometry, in explicit analytical form for cylindrical geometry, and by numerical integration of Eqn. (2) for spherical geometry. It has been shown[29] that for the symmetrical geometries under discussion the variation of δ_{cr} with Bi can be approximated (to an accuracy equal to or better than 10%) in the form

$$\delta_{cr} \simeq \delta_n \varphi(\mathrm{Bi}),$$

where δ_{cr} is the critical value of the parameter δ for Bi = ∞, which depends on the form of the function (according to Frank-Kamenetskii's theory, $\delta_0 = 0.88$, $\delta_1 = 2.00$, $\delta_2 = 3.32$), and

$$\varphi(\mathrm{Bi}) = \frac{\mathrm{Bi}}{2}\left(\sqrt{\mathrm{Bi}^2+4} - \mathrm{Bi}\right)\exp\frac{\sqrt{\mathrm{Bi}^2+4} - \mathrm{Bi} - 2}{\mathrm{Bi}}, \qquad (3)$$

is a universal parameter, independent of the form of the function.

The significance of recent researches[29,30] lies in the fact firstly that they provide means for calculating critical thermal explosion conditions in many practical cases, and secondly that they are able to unify the theories of Semenov and Frank-Kamenetskii by eliminating the apparent contradiction between their respective models of the temperature distribution in the system. This work has allowed a re-evaluation of the original and simplest theory of thermal explosions.

The rules applying to the transition from the Semenov to the Frank-Kamenetskii régime are illustrated in Figs. 3 and 4. The latter diagram is reproduced from a paper by Gray and Harper[32].

Many workers[29,31,33,34] have discussed various approximate methods for calculating the variation of δ_{cr} with Bi. The simplest of these[29] is based on Frank-Kamenetskii's

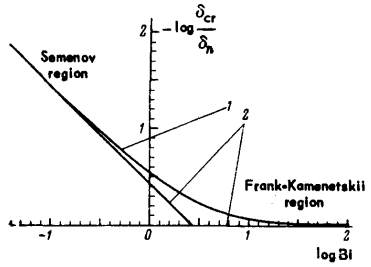

Fig. 3. 1) General form of the function $\varphi(Bi)$; 2) asymptotes according to Semenov and Frank-Kamenetskii[29].

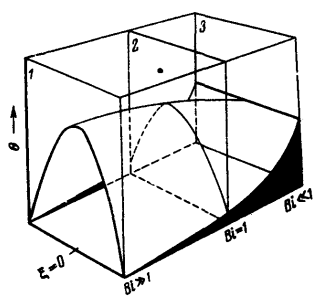

Fig. 4. Steady-state temperature distribution at the thermal explosion limit[32].

concept of an effective internal heat transmission coefficient, and on his rule for combining thermal resistances. The resulting formula

$$\frac{1}{\delta_{cr}} = \frac{1}{\delta_n} + \frac{e}{(1+n)\,Bi},$$

is very convenient and gives tolerably accurate results (~ 15% in the most unfavourable case).

One of the main problems of the steady-state theory is the calculation of δ_{cr} for bodies of complicated geometrical form (the so-called geometrical problems of the theory of thermal explosions). The mathematical difficulties of the calculation, especially for three dimensional regions, are obvious. Starting from various physical and mathematical considerations, a simpler procedure for approximately calculating the critical conditions has been obtained[12,31,34]: according to this, $\delta_{cr} \simeq \mu_1^2/e$, where μ_1^2 is the first eigenvalue of the homogeneous linear equation of thermal conduction

$$\Delta\theta + \mu^2\theta = 0,$$

for the region under consideration, with the appropriate boundary conditions. This method has been used[12,35] to calculate δ_{cr} for a hollow cylinder, a cylinder of finite length, a cylindrical sector, and a cube. The results have been shown to agree satisfactorily with the numerical integration of the original equation of thermal explosion. It is not yet clear, however, whether the method can be applied to the calculation of critical conditions for complicated, unsymmetrical shapes.

Analytical solutions of Eqn. (2) have been obtained for the limiting cases of $\beta \to 0$. The possibility of considering this case followed from Semenov's theory, and was put on a physical basis by Frank-Kamenetskii (the so-called Frank-Kamenetskii exponential transformation). Using Semenov's theory, and the numerical calculations of Parks[36], we can introduce corrections for the quantity β:

$$\delta_{cr}(\beta) \simeq \delta_{cr}(0)(1+\beta),\quad \theta_{cr}(\beta) \simeq \theta_{cr}(0)(1+2\beta),$$

where θ_{cr} is the initial heating preceding explosion. Hence we can estimate the error of the formulae obtained in the steady-state theory for $\beta = 0$:

$$\Delta_1 = \frac{\delta_{cr}(\beta) - \delta_{cr}(0)}{\delta_{cr}(0)} \simeq \beta;\ \Delta_2 = \frac{\theta_{cr}(\beta) - \theta_{cr}(0)}{\theta_{cr}(0)} \simeq 2\beta.$$

For the commonly encountered values of β, the error in the calculation of δ_{cr} is 1–5%, whilst the error in θ_{cr} is 2–10%.

3. Non-Stationary Theory of Thermal Explosions

In its classical form, the non-stationary theory of thermal explosions studies the variation with time in the heating-up of the system and in the extent of chemical reaction by analysing equations set up in terms of quantities which are averaged over the entire volume (or on the assumption that there is no temperature distribution within the reaction zone). The initial temperature is assumed equal to the temperature of the surroundings. Thus

$$\frac{d\theta}{d\tau} = \varphi(\eta)\exp\frac{\theta}{1+\beta\theta} - \frac{1}{\varkappa}\theta,$$

$$\frac{d\eta}{d\tau} = \gamma\varphi(\eta)\exp\frac{\theta}{1+\beta\theta}, \qquad (4)$$

$$\tau = 0,\ \theta = 0,\ \eta = 0,$$

where

$$\varkappa = \frac{Q}{\alpha\dfrac{S}{V}}\frac{E}{RT_0^2}k_0\exp\left(-\frac{E}{RT_0}\right),$$

is Semenov's parameter, V being the volume occupied by the reacting substance, and S the area of the heat-emitting surface.

In the non-stationary theory, explosion conditions are identified with a progressive increase in heating up. The main objective of the non-stationary theory is to study simple reactions which are not autocatalytic under isothermal conditions.

The classical non-stationary theory was developed in papers by Todes and his coworkers[2,4,5]. It gives an analytical solution of the simplest non-stationary problem (the adiabatic explosion), as well as results of the numerical integration of a set of equations of type (4), whence it is possible to analyse the development of heating-up preceding the explosion and to draw important conclusions concerning the kinetic features of the phenomenon. However, the authors used laborious manual computation and inconvenient dimensionless parameters, and were therefore unable to arrive at a satisfactory quantitative generalisation of their results.

The hope of obtaining formulae for calculating the induction period has led to a number of investigation[32,37-39], aimed mainly at an analytical solution of simplified non-stationary equations. A common feature of all these researches is the attempt to express the Arrhenius exponent in terms of a power series. In our opinion, none of these investigations has produced a computational procedure applicable to the non-stationary theory, although

several useful results have been obtained with the help of Gray and Harper's quadratic approximation.

One of the problems which concern the non-stationary theory is the displacement of the thermal explosion limit caused by the combustion of material during the induction period, i.e. the variation of δ_{cr} with γ. For normal, non-degenerate thermal explosion régimes ($\gamma < 10^{-2}$), this variation merely introduces a correction, but it becomes very significant for large values of γ (systems with a relatively small heat of reaction). The variation of δ_{cr} with γ was first calculated by Frank-Kamenetskii, who discussed the non-stationary explosion system close to the limit and showed that

$$\delta_{cr} \simeq \delta_n [1 + 1.39 (m\gamma)^{\frac{2}{3}}].$$

This formula has enjoyed wide popularity, but it has recently been pointed out [40,41] that the value of 1.39 given for the coefficient is erroneous. The correct value of this coefficient in Frank-Kamenetskii's solution is 2.7. A comparison of various reported variations of δ_{cr} as a function of γ is made in Gray and Lee's note [41].

Practically all the papers mentioned above have considered a set of equations in which the temperature distribution in the reaction zone is ignored. A detailed analysis of non-stationary solutions to the general system of equations (1) for thermal explosion régimes ($\theta_{init} = 0$) has been carried out [42] by numerical integration on an electronic computer. This work involved many calculations over a wide range of values of all the parameters, and produced results of relatively high accuracy. This enabled the authors to discuss a number of "fine effects" in the non-stationary model of thermal explosions which had not been given due prominence in the classical theory, and to put forward a quantitative generalisation of the calculated critical conditions and induction periods. Basing ourselves on that paper [42] and on earlier work, we shall note the basic features of the phenomenon revealed by an analysis of the non-stationary equations.

The theory of thermal explosions deals with two clearly distinguishable régimes, comprising reactions occurring under non-isothermal conditions with relatively little heating-up, and reactions undergoing progressive autocatalysis leading to explosion. In the model for a zero-order reaction, $\gamma \to 0$ or $\varphi(\eta) \equiv 1$, the transition from one régime to the other occurs abruptly at $\delta = \delta_{cr}$, and a maximum value of the steady-state heating-up θ_{cr} exists. When combustion of the reactant occurs, the mathematical discontinuity separating these two régimes disappears. The transition from one régime to the other becomes continuous. Continuity of the transition is conveniently demonstrated by the plot of the maximum (with respect to time) heating-up at the centre of the system θ_m against the parameter δ (Fig. 5).

Thus, analysis of the non-stationary equations leads to the conclusion that there are no critical conditions in the mathematical sense. Likewise, there is no heating-up preceding explosion, a characteristic introduced in the steady-state theory. It is evident from Fig. 5 that some régimes can have $\theta_m > \theta_{cr}$ and yet not qualify as explosions. The width of the transition region in terms of δ depends on the value of γ: the larger γ, the wider is the transition region. By the very nature of the phenomenon, thermal explosion corresponds to a narrow transition region (usually $\gamma = 10^{-2}$–10^{-3}), and the critical conditions have a clear physical significance. At high values of γ

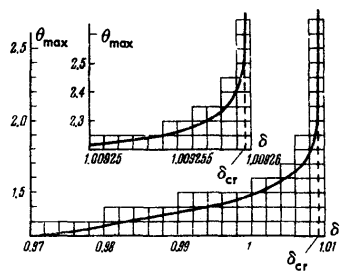

Fig. 5. Variation of the maximum heating-up of the system with the parameter δ when $n = 1$, $\theta_{init} = 0$, Bi = 2, $\beta = 0.03$, and $\gamma = 0.005$ for a first-order reaction [42]. The values of δ_{cr} and θ_m calculated from the steady-state theory are 0.95 and 1.35 respectively.

the phenomenon of thermal explosion becomes degenerate, and critical conditions become meaningless in the physical as well as in the mathematical sense. The transition from normal to degenerate régimes of thermal explosion is also continuous. If we definite the conditions for normal régimes as

$$\delta_*(\gamma) - \delta_{cr}(0) \ll \delta_{cr}(0),$$

where $d^2\theta_m(\delta_*)/d\delta^2 = 0$, we can take the quantity δ_* to be the critical value of the parameter δ in the presence of combustion.

We shall now consider the problem of determining the induction period τ_{ind}, which has been defined [4,11,43] as the time for completion of the heating-up preceding explosion θ_{cr}. It was assumed that the time of reaction $\theta > \theta_{cr}$ is much shorter than the induction period. This definition is inaccurate, since firstly there is no pre-explosion heating-up as such, and therefore the time needed to reach θ_{cr} is not a characteristic quantity, and secondly the time during which the reaction proceeds at $\theta > \theta_{cr}$ cannot be neglected. Even in the most favourable case (under adiabatic conditions) this time amounts to ~ 30% of the total time lag [42]. As the limit is approached, this value increases rapidly and becomes greater than the time of the heating-up preceding explosion.

Surprisingly, this definition of the induction period originated from a curious error made by Todes. When analysing his calculated θ–τ curve (Fig. 5 of Ref. 4, p. 874), Todes stated in the text that the increase in heating-up from the value corresponding to θ_{cr} to the highest value ($\theta_m \simeq 1/\gamma$ in our symbols) "occurs at almost constant time, i.e. practically instantaneously". This conclusion is based on a misunderstanding, and certainly does not follow from the published curve. This erroneous statement then found its way into Semenov's review [11], where it forms the basis of the definition of induction period: "The time elapsing between the beginning of the reaction and the heating-up preceding explosion is called the induction period. It is practically identical with the time between the beginning of the reaction and the explosion" (Ref. 11, p. 275). This error by Todes was pointed out to the present writers by Barzykin.

It would seem more correct to identify the induction period with the time needed to reach the maximum rate of a non-isothermal reaction [42]. This definition of the induction period gives a more accurate impression of the

time needed for the onset of explosion, and gives an insight into the transition region in terms of the time characteristic. The function $\tau_{ind}(\delta)$ has a maximum at the value of δ corresponding to δ_{cr}. As $\delta \rightarrow \delta_{cr}$ (from either side) τ_{ind} rises steeply towards its maximum value τ_{cr}.

The following empirical formulae have been derived[42] for calculating δ_{cr} and τ_{ind} for a first-order reaction, which quantitatively reflect the basic features of thermal explosions: (*a*) the critical condition

$$\delta_{cr} = \delta_n \varphi\,(\mathrm{Bi}(1 + 2.4\,\gamma^{3/4})(1 + \beta),$$

where $\varphi(\mathrm{Bi})$ has the form of Eqn. (3); (*b*) the induction period ($1.1 < \Delta < 10$)

$$\tau_{ind} = \tau_{av}\,(1 - K),$$

where

$$\tau_{av} = \left[1 + 0.62\,\frac{1 - 4\,\Delta^{-3}\sqrt{\gamma}}{(\Delta - 0.95)^{0.9}}\right](1 + 2\beta),$$

$$K = \frac{[1 + 1.5(1 - 0.1\,\Delta)n]\,\mathrm{Bi}}{16(1 + \mathrm{Bi})},$$

and $\Delta = \delta/\delta_{cr}$ is the relative departure from the thermal explosion limit.

The function τ_{av}, obtained by solving the system of equations (4), which disregards the temperature distribution in the reaction zone, expresses the basic variation of the induction period with Δ for different values of β and γ. The function K describes the variation in induction period resulting from geometrical shape and from heat exchange, i.e. the extra information obtained by considering the system of equations (1) in comparison with (4). The quantity K expresses the error involved in calculating the induction period from the averaged set of equations, and is essentially a criterion of the accuracy of the non-stationary theory in the classical treatment. The largest error occurs with $n = 2$, $\mathrm{Bi} = \infty$, and $\Delta \rightarrow 1$: under these conditions $K \simeq 0.23$. A small value of K (which makes averaging possible) is obtained when the heating-up of the system in the pre-explosion period is not too large. We should stress that the averaging can lead to significantly large errors when degenerate régimes are considered (β and γ relatively large) or when $\theta_{init} \neq 0$.

4. Quasistationary Theory of Thermal Explosions

The non-stationary theory is essentially the most general theory of thermal explosions, because its methods (based mainly on numerical integration) give a comprehensive picture of the phenomenon and allow calculation of all the characteristics for different reactions under different conditions. The critical conditions for thermal explosion is simple, non-autocatalytic reactions can also be determined using the approach of the steady-state theory. Thermal explosions in reactions showing isothermal autocatalysis are considered in the quasistationary theory.

The quasistationary procedure for calculating the characteristics was unknown in the classical theory. Todes and Melent'ev discussed the thermal explosion of autocatalytic reactions on the basis of numerical integration of the equations, and showed in particular that the critical condition is of the same form as for a zero-order reaction provided that the rate constant is replaced by the maximum reaction velocity under isothermal conditions. Semenov[11] suggested isothermal computation for calculating the induction period.

The quasistationary theory of thermal explosions has been developed by the present writers[44]; it is based on the specific features of autocatalytic reactions occurring under non-isothermal conditions. The quasistationary theory deals also with régimes under which the initial reaction rate does not satisfy explosion conditions. It is well known that in these circumstances an explosion can develop at high degrees of conversion. The course of the process preceding explosion in autocatalytic reactions can be envisaged[44] as involving in the initial stages on essentially non-stationary thermal régime, which continues until the initial rate of heat evolution is balanced by the heat losses. The resulting equilibrium situation then begins to be displaced by isothermal autocatalysis of the reaction, leading to an increase in the temperature of the system: thus, the higher the rate of heat evolution, the greater is the steady-state heating-up. Under this régime practically the whole of the heat evolved by the reaction is lost to the surrounding medium, the rate at which heat accumulates in the system is small compared with the rate of evolution of heat, and the heating-up increases slowly (quasi-stationarily). When the reaction rate reaches a value which satisfies the condition for explosion, the quasi-stationary régime is disturbed, and gradual autocatalysis of the reaction sets in, leading to an explosion. If, however, the maximum rate of the isothermal reaction does not satisfy the explosion condition, the reaction goes to completion under a quasistationary régime. The induction period in systems showing appreciable isothermal self-acceleration is practically equal to the time of the quasistationary stage of the reaction, and can be calculated by means of the quasistationary model.

A procedure for calculating all the basic characteristics of the thermal explosion in self-accelerating reactions has been proposed[44] involving solution of the system of equations (4) in the quasistationary approximation (in which the term $d\theta/d\tau$ is assumed to vanish), for the case of an autocatalytic first-order reaction $\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$. The conditions under which a quasistationary régime can arise are also discussed, a criterion for a quasistationary reaction being obtained. The region of existence of the quasistationary régime (and therefore the applicability of the quasistationary theory) is illustrated by the $\kappa - 1/\eta_0$ diagram (Fig. 6). The boundary of the quasistationary region (the quantity κ_{qs}) is arbitrary, because the quasi-stationary régime becomes gradually degenerate as we depart from the thermal explosion limit. The value of κ_{qs} depends on γ: the smaller γ, the greater is κ_{qs}, and the wider is the region of quasistationary pre-explosion régime.

The general system of equations (1) has been integrated numerically[45] on an electronic computer for $\varphi(\eta) = (\eta + \eta_0) \cdot (1 - \eta)$ and $\theta_{init} = 0$. It is found that the "fine effects" observed in the non-stationary theory for simple reactions (continuous variation of θ_m with δ, presence of a maximum induction period close to δ_{cr}) occur also in autocatalytic reactions, but are not so clearly developed. Fig. 7 shows the non-stationary "surge" of the induction period, superimposed on the general quasistationary tendency for τ_{ind} to decrease. Since this effect is relatively small, the quantity τ_* calculated by the quasistationary theory can be identified with the induction period at the thermal explosion limit. Calculation shows that τ_{ind} at constant Δ is very insensitive to n and Bi, so that the error involved in applying the averaged system of equations (4) to autocatalytic reactions is insignificant (much less than the quantity K as calculated in the non-stationary theory). Therefore the formula obtained by Khudyaev[46] for the particular case of

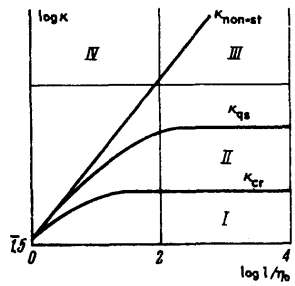

Fig. 6. Different thermal explosion régimes for an autocatalytic reaction, $\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$: I) quasistationary régime below the thermal explosion limit; II) quasi-stationary régime below the thermal explosion limit; III) degenerate quasi-stationary régime; IV) effectively non-stationary reaction.

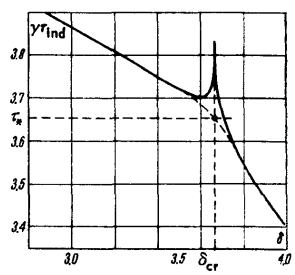

Fig. 7. Variation with δ of the induction period near the limit for $\varphi(\eta) = (\eta + \eta_0)$. $(1 - \eta)$, $n = 1$, $\eta_0 = 0.01$, $\gamma = 0.005$, $\beta = 0$, and Bi = 2.[45]

$n = 1$, Bi $\to \infty$, can be recommended for calculating the induction period of an autocatalytic first-order reaction:

$$\tau_{ind} = \frac{1}{\gamma(1+\eta_0)}\left\{\ln\frac{\sqrt{\tau_1}}{\eta_0} + \frac{1}{2}\ln\frac{(1-\eta_0)\tau_2+\tau_3}{2} + \tau_4 - \sqrt{\Delta}\ln\frac{\sqrt{\Delta}(1-\eta_0)+\tau_2}{1+\eta_0} - \right.$$
$$\left. - \Delta\left(\frac{1}{1+\eta_0} + \frac{1}{1+\tau_1}\right)\right\}$$

$$\tau_1 = 1 \text{ for } \Delta \leqslant 1$$

$$\tau_1 = 2[\Delta - \sqrt{\Delta(\Delta-1)}] - 1 \text{ for } \Delta \geqslant 1;\quad \tau_2 = \sqrt{(1+\eta_0)^2 - 4\Delta\eta_0},$$
$$\tau_3 = (1+\eta_0)^2 - 2(\Delta+1)\eta_0;\ \tau_4 = \frac{1}{2}\left|\sqrt{\Delta} - 1\right|\ln\left|\Delta - 1\right|.$$

At the thermal explosion limit the formula takes the simple form

$$\tau_{cr} = \frac{1}{\gamma(1+\eta_0)}\left[\ln\frac{1+\eta_0}{2\eta_0} - \frac{1-\eta_0}{2(1+\eta_0)}\right].$$

It is interesting to note that, in a simpler case than that considered by Khudyaev, not taking account of the temperature distribution in the reaction zone, τ_{ind} is expressed by a definite integral which cannot be resolved into elementary functions.

The quasistationary theory is now widely used in experimental studies of thermal explosions in condensed phases.

III. THERMAL EXPLOSION RÉGIMES NOT DESCRIBED BY THE CLASSICAL THEORY

In this Section we shall consider some thermal explosion processes whose description does not fall within the scope of the classical theory based on the simple model formulated at the beginning of this Review. These include thermal explosion régimes with applied heating or cooling, in the presence of external heat exchange by conduction, with local application of a heat pulse, etc.

1. Dynamic Thermal Explosion Régimes in the Presence of Heating and Cooling

We shall call thermal explosion régimes involving variation in the temperature T_0 of the surroundings according to a given time law "dynamic régimes", to distinguish them from the static régimes (T_0 = const) considered in the classical theory. The study of dynamic régimes is of considerable interest from many points of view, since it allows us: (1) to develop and generalise the quasistationary theory of thermal explosions, and to supplement it with an analysis of constrained quasistationary régimes involving a shift in the position of balance between the supply and the removal of heat resulting from variation in T_0; (2) to propose dynamic methods for the experimental measurement of thermal explosion characteristics (including rapid, approximate methods), which are sometimes more satisfactory than the static methods; and (3) to solve some applied problems of possible explosion under actual conditions of variation in T_0, which arise in the practical employment of explosive systems (e.g. in the application of explosives for "torpedoing" and for drilling oil-wells[47]).

A theory of thermal explosions under conditions of linearly varying T_0 (both heating and cooling) has been developed[48-51] on the basis of solving the systems of equations (1) and (4) in conjuction with the time law for the change in temperature of the surroundings

$$T_0 = T_{init} + wt,$$

(where w is the rate of change of the temperature). Two cases of particular interest were examined —

$$T_{init} \ll T_{0,cr},\ w > 0 \text{ — heating},$$
$$T_{init} > T_{0,cr},\ w < 0 \text{ — cooling},$$

where $T_{0,cr}$ is the critical temperature for thermal explosion under static conditions (a quantity known from the classical theory).

Under the dynamic régimes T_0 is not a constant, and it cannot therefore appear among the dimensionless parameters of the problem. The quantity $T_{0,cr}$ was found to be a convenient scale factor for the temperature. The fundamental parameter of the dynamic problem

$$\left(\omega = w\frac{E}{RT_{0,cr}^2}\frac{1}{k_0}\exp\right)\frac{E}{RT_{0,cr}},$$

is the ratio of the scale factors for reaction time and for temperature change.

This is, essentially, the dynamic analogue of the parameters proposed by Semenov and by Frank-Kamenetskii. The basic dynamic characteristic is the temperature of the surroundings at which explosion occurs (analogous to the induction period).

Let us briefly examine, on the basis of recent results[48-51], the development of explosions under conditions of heating and of cooling.

On heating, provided that $T_{init} \ll T_{0,cr}$, the system behaves at first as an inert substance, and the temperature in it develops a steady-state lag with respect to T_0. On further heating, the reaction begins to evolve heat, the lag disappears, and the temperature within the system rises above that of the surroundings. For a zero-order reaction this temperature rise in the system leads to explosion. In real systems, there is always a critical rate of heating ω_{cr}, such that when $\omega < \omega_{cr}$ the reaction goes smoothly to completion without excessive overheating, whereas when $\omega > \omega_{cr}$ an explosion occurs.

We should stress that the appearance of critical conditions on heating is fundamentally due to burning off of the material, whereas under the static régime burning off merely introduces a correction. In the neighbourhood of ω_{cr} various types of reaction show a region of quasi-stationary reaction characterised by a considerable extent of pre-explosion transformation (as with autocatalytic reactions in the static case). At large values of ω we find a transition from thermal explosion to ignition (with a clearly defined value of ω'_{cr}), which is in a qualitative sense entirely analogous to the static régime [51]. An approximate analytical procedure, based on quasistationary concepts, has been developed for the calculation of ω_{cr} and other characteristics in the neighbourhood of the limit [48,49].

The pattern of thermal explosion on cooling (when $T_{init} > T_{0,cr}$ always) depends essentially on whether the thermal self-acceleration régime at T_{init} is quasistationary or non-stationary under static conditions. If the former, the initial reaction velocity at T_{init} does not satisfy the explosion condition, and this condition may result from competition between two opposing factors — isothermal self-acceleration of the reaction and the decrease in reaction rate caused by the fall in temperature — in which conditions the extent of the pre-explosion reaction η_{expl} is always less than the extent of reaction corresponding to the maximum rate under isothermal conditions (in other words, the burning-off of material actually does not play a major part). In the second case the explosion condition is satisfied from the beginning, and the thermal balance is predetermined by the competition between the fast development of the pre-explosion process and the decrease in reaction velocity due to the fall in temperature. At high values of T_{init} an explosion invariably occurs, however high the cooling rate. A quasistationary calculation of the characteristics and a numerical integration of the system of equations (4), have been made [50] for the case of $\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$. Studies under a cooling régime are very interesting from the point of view of technique, because heating the substance above the critical temperature followed by cooling allows the critical conditions for thermal explosion to be investigated with a much shorter induction period.

At the moment, the framework of the dynamic theory still lacks the unified and definitive form which characterises the classical thoey. In particular, it needs more mathematical work on the general dynamic set of equations for thermal explosion, based on explicit functions of time both in the equations themselves and in the boundary conditions. The principles needed to develop dynamic methods for studying thermal explosions, which will allow experimental investigations to be completed in a much shorter time (thus overcoming the difficulties arising from long induction periods), have not yet been formulated.

2. Thermal Explosions under Conditions of Conductive Heat Transfer in the Surrounding Medium

The solution of the problem in the classical formulation ignores heat-transfer processes in the external medium. The role of the surroundings is characterised uniquely by the boundary conditions. Yet, there are many thermal explosion régimes under which it is essential to consider the transfer of heat in the external medium. This is particularly true of systems surrounded by non-mobile media (a condensed phase in a solid block, a gas or a liquid in a thick-walled vessel, fine particles of a condensed substance in a gas or a liquid, a localised explosive impurity, etc.). To describe thermal explosions in systems of this type we must consider the equation for heat conduction in the surrounding medium as well as the system of equations for the internal region — of type (1) or of type (4) — in other words, we must solve the conjugate problem.

Grigor'ev and coworkers [52] have discussed this problem by considering the ignition of spherical particles in a hot gas, and have also made a more general study [53] of the critical thermal explosion conditions. They show, in particular, that the conjugate problem is equivalent to a boundary problem in which the conditions at the boundary of the inner region are expressed by integro-differential relations in the form of a Duhamel integral. Critical conditions have been calculated for $n = 0$, 1, and 2, and $\varphi(\eta) = 1 - \eta$, by numerical integration on an electronic computer.

Thermal explosions involving heat loss to the surroundings by conduction are shown [53] to have a number of specific features, summarised as follows:

1. The quantitative aspects of the phenomenon depend essentially on the geometry of the system. Of the three shapes which were considered, only the spherical case leads (under certain conditions) to a steady-state régime, thus allowing the approach of steady-state theory to be used. In the planar and the cylindrical geometries (excluding the limiting case of constant surface temperature) the critical conditions are determined mainly by the burning-off of the material (as in the case of linearly rising temperature).

2. The relationship between internal and external heat transfer is independent of the geometrical size of the system. It follows that the transition from the limiting case of constant temperature at the surface of the reacting substance to the limiting case of absence of temperature gradients in the reaction zone is also unaffected by the size of the system.

3. A reaction which is not autocatalytic under isothermal conditions can occur under a quasistationary régime close to the self-ignition limit during the pre-explosion period: this arises from the decrease in the effective coefficient of heat transfer from the surface of the reactant into the external medium. Hence it is possible, in principle, to develop a quasistationary theory of the phenomenon which deals with régimes under which the position of balance between heat supply and heat losses is a slowly varying function of some parameter. In autocatalytic reactions the shift in equilibrium is caused by an isothermal increase in reaction rate; under dynamic (heating) régimes it is caused by the increase in temperature of the surrounding medium; and the present case it is caused by a decrease in the effective heat-transfer coefficient. In consequence

of the quasistationary régime we find, as usual, extensive pre-explosion reaction, which is a characteristic of the present case.

Studies of thermal explosion in the present of conductive heat transfer in the external medium are still in their early stages: it is not surprising, therefore, that many of the problems have not been satisfactorily solved.

3. Localised Thermal Explosion Régimes

If, owing to special circumstances, the initial reaction in an explosive system does not proceed uniformly throughout the volume, the onset of thermal explosion can show a localised character. In the problems of explosion with a localised focus we can again distinguish (though arbitrarily) between an internal and an external region, and discuss the course of the chemical reaction in the two regions. The localised problem includes two aspects — the explosion of the local centre itself and the focal excitation of a self-propagating reaction in the medium — the former aspect being proper to the theory of explosions. We shall consider two types of focus —

1. A chemical focus, when the temperature of the focus is initially the same as that of the medium, but the kinetic parameters of the reaction are different.

2. A thermal focus, at which the temperature is higher than that of the medium, while the kinetic parameters of the reaction are the same.

The first type of focus includes cases of localised impurities of one explosive substance in another. The second type arises from external (non-thermal) influences on explosive systems.

The cases of localised explosion discussed in the literature[54-58] deal exclusively with the thermal type of focus, considered on the simplest model of a Π-shaped focus. Some workers[54,56,57] have attempted an approximate analytical calculation of the critical conditions: others[55,58] give the results of numerical solution of the equations, generalised to a dimensionless form. The basic parameters of the problem are

$$\delta = \frac{Q}{\lambda}\frac{E}{RT_0^2}r^2k_0\exp\left(-\frac{E}{RT_0}\right)$$ Frank-Kamenetskii's parameter,

$$\theta_0 = \frac{E}{RT_0^2}(T_0 - T_1)$$ initial temperature differential of the focus,

where T_0 is the initial temperature of the focus and T_1 is the temperature of the substance.

The critical explosion condition for the focus is of the form $\delta_{cr} = f_n(\theta_0)$. Merzhanov[58] has reviewed the work devoted to the evaluation of this function. As Table 2 shows, the approximate theories of Zinn[54], Friedman[56], and Boddington[57] lead to an incorrect form of the function $\delta_n^{init}(\theta_0)$, because they do not take into account the most essential feature of thermal explosion with a thermal focus, which is the presence of large temperature gradients in the focus. We have as yet no satisfactory approximate theory of this phenomenon.

The problem of thermal explosion of a thermal focus is of great importance to the theory, now being developed, of the sensitivity of explosive systems to external (non-thermal) influences. The expressions obtained for $\delta_{cr}(\theta_0)$ are adequate for the present level of development of the sensitivity theory and are widely used in tentative calculations of the critical size (or temperature) of the focus.

4. Hydrodynamic Problems of Thermal Explosion Theory

Hydrodynamic problems arise in the discussion of thermal explosion régimes under which the reactant is in a state of motion. The two most interesting aspects of the problem are the forced flow of viscous liquids and convection in low-viscosity liquids. In the former case the main interest lies in the dissipation of the energy of motion, and two types of heat source — chemical and mechanical — have to be considered in the analysis of the thermal explosion. Nothing has yet been published on the theory of thermal explosions with mechanical sources of heat. However, a recent series of papers[59-62] has a bearing on the problem, since it deals with the so-called hydrodynamic thermal explosion. From a theoretical analysis of the flow of a chemically inert, viscous liquid under the influence of a pressure difference it is shown that under certain conditions the heat evolved by internal friction is unable to pass into the surrounding medium, and causes the temperature to rise at an increasing rate: the analogy with thermal explosions is evident. Bostandzhiyan and his coworkers[60] have calculated the critical conditions for hydrodynamic explosion, and discussed the analogy with thermal explosions of chemical origin. It is interesting to note that a hydrodynamic explosion can occur only under forced flow conditions, whereas in free flow there are always steady-state régimes with different amounts of heating-up[59,61]. The ideas and methods of the theory of hydrodynamic explosion can be useful in the analysis of the flow of a chemically reacting liquid, because in this case the basic characteristics of the phenomenon — the critical condition and the induction period — may be independent of the kinetics of the chemical reaction, being determined by hydrodynamic factors.

The second aspect of the hydrodynamic problem is concerned with the convection mechanism of heat transfer in a reacting liquid. This question has been discussed in the literature for many years, but a satisfactory solution is still lacking because serious difficulties arise in describing the process. The simplest problem (in essence not a hydrodynamic one) involving convective heat transport — that of thermal explosion in a gas stream — has been discussed by Merzhanov and Filonenko[63], and the results have been applied in the theory of the combustion of condensed phases.

TABLE 2.

Reference		54	56	57	55, 58
General form of function $f_n(\theta_0)$		a_n	$b_n\,\theta_0$	$c_n\,\theta_0^2$	$d_n\,(\ln\theta_0)^m$
Values of the constants	$n=0$	$a_0=8$	$b_0=1$	$c_0=0.159$	$d_0=2.66$, $m_0=1.3$
	$n=1$	—	—	$c_1=0.637$	$d_1=7.39$, $m_1=0.83$
	$n=2$	$a_2=25$	—	$c_2=1.433$	$d_2=12.1$, $m_2=0.6$

IV. METHODS OF EXPERIMENTAL INVESTIGATION AND TESTS OF THE THEORY

The basic requirement of methods for the experimental study of thermal explosion processes is that the main parameters which determine the course of the reaction should be clearly defined and reproducible in successive experiments. These include the temperature of the surrounding medium, the shape and size of the vessel (or specimen), the conditions of heat exchange with the surroundings, the pressure, and the density (with condensed phases).

With gaseous systems the most commonly used methods are admission to a heated vessel and adiabatic compression. Frank-Kamenetskii's monograph [12] discusses the problems arising during experimental tests of the classical theory of thermal explosion in various gaseous mixtures.

The present writers, in collaboration with Abramov [64], proposed the use of thermal analysis for the study of thermal explosions in condensed substances, and have subsequently developed the method further [65-67]. The method consists essentially in placing the experimental substance in a cylindrical reaction vessel, heated by a thermostatically controlled heat-transfer agent, the coefficient of heat transfer to which is measured in preliminary experiments. The limiting cases of constant temperature at the inner surface of the vessel and of absence of temperature gradients in the material can be realised in various ways. Heat evolution in the material is recorded by a differential thermocouple. The results are analysed from plots of the heating effect against time, which give information on the critical conditions, subexplosive heating, induction periods, and heating times of the system. If the substance does not contain temperature gradients, the kinetic characteristics of the heat evolution can be calculated from the differential thermograms [68]. Different variants of the method have been developed (for different ranges of temperature and size, for different conditions of heat exchange with the surroundings, for static and dynamic régimes, for high pressures of an inert gas).

The thermographic method has been used in an extensive series of experimental investigations. We shall consider some of the results obtained in experimental tests of the theory in the specific case of the thermal explosion of DINA and tetryl in the liquid phase. The experimental conditions were chosen so that temperature gradients in the reaction zone were negligible [65,66]. The results of the experiment, and those of an absolute calculation based on independent kinetic [69,70] and thermophysical data, presented in Tables 3–5, illustrate the great precision of the theoretical description of the phenomenon. It is interesting to note that the critical conditions for DINA were calculated by Semenov's theory, because the experimental conditions agreed with the model assumed by Senemov. Thus, the simplest model of the thermal explosion phenomenon, proposed by Semenov and still lacking a rigid quantitative basis for the case of gases (owing to the presence of temperature distributions in the reaction volume), was first realised in a thermal decomposition in the liquid phase.

Another method [52,71] for the experimental study of thermal explosions in condensed phases uses a spherical particle of the material in a heated gas. The experiments are carried out at low Reynolds and Grashof numbers, and therefore the heat exchange between particle and gas can be characterised by the heat-transfer coefficient $\alpha = \lambda_g/r$,

TABLE 3.

d, mm	$\alpha\frac{S}{V}$, cal cm^{-3} × × s^{-1} deg^{-1}	l/d	$T_{0,cr}$, °C calc.	$T_{0,cr}$, °C expt.	Pre-explosion heating ΔT_{cr}, deg calc.	Pre-explosion heating ΔT_{cr}, deg expt.	Experimental conditions
6.2	$1.4\cdot10^{-3}$	2	157	158	8.3	11	weak heat exchange with surrounding medium
8.5	$7\cdot10^{-3}$	2	152	152.5	7.95	8	
10.3	$3.1\cdot10^{-3}$	2	145	145.5	7.7	9	
10.3	$4.7\cdot10^{-3}$	1	147.5	148.5	7.8	9	
12.7	$3.5\cdot10^{-3}$	1	146	147.5	7.75	6	
32	$1.35\cdot10^{-2}$	2	160	162	8.25	9	artificial stirring of the material
36.5	$1.15\cdot10^{-2}$	2	157	159	8.15	10	
37.5	$1.05\cdot10^{-2}$	2	156	158	8.10	8	
49	$1.20\cdot10^{-2}$	2	154	153	8.05	8	
62	$1.15\cdot10^{-2}$	1	152	152	7.95	9	

TABLE 4.

d, mm	$\alpha\frac{S}{V}$, cal cm^{-3} × × s^{-1} deg^{-1}	l/d	$T_{0,cr}$, °C calc.	$T_{0,cr}$, °C expt.	ΔT_{cr}, deg calc.	ΔT_{cr}, deg expt.
6.1	$1.4\cdot10^{-3}$	2	155	151.5	9.5	8
8.4	$7.1\cdot10^{-3}$	2	149	148.5	9.4	12
8.7	$3\cdot10^{-3}$	2	140	139.5	8.9	10
11.7	$2.7\cdot10^{-3}$	2	139	139.5	8.9	9

TABLE 5.

d, mm	$T_{0,cr}$, °C	t_{cr}, min calc.	t_{cr}, min expt.	d, mm	$T_{0,cr}$, °C	t_{cr}, min calc.	t_{cr}, min expt.
6.1	151.5	70	60	8.5	143.5	170	160
8.4	148.5	100	100	11	141	225	240
9.8	148.5	100	95	8.7	139.5	275	280
8.1	148	115	110	11.7	139.5	275	300

where λ_g is the thermal conductivity of the gas and r is the radius of the particle. Under these conditions, calculation shows that temperature gradients within the particle are negligible. The thermal explosion of the particle is detected by an optical method, using the incandescence of the explosion products. The critical conditions and the total time lag before the explosion (including the heating-up stage) can be determined from these experiments. The theory of the method [52] allows adequate analysis of the experimental results. It is important to remember that flameless detonation, which cannot be observed, may occur near the limit. However, the presence of this régime can be discovered by a series of determinations of the critical conditions in different gases. The preparation of the material in the form of spherical particles often presents special problems.

We shall examine the results of a study [52], by this method, of the thermal explosion of pyroxylin. Fig. 8 shows the variation of the critical temperature as a function of particle size in air and in argon, and Fig. 9 shows the variation of the time lag with particle size and with gas temperature, expressed in dimensionless quantities.

From the critical condition the kinetic constants were evaluated, and from these the time lag was calculated. The agreement between calculated and experimental results is satisfactory.

The method based on the thermal explosion of a particle in a heated gas is of interest from the point of view of the study of ignition mechanisms at high temperatures, and of the measurement of effective kinetic parameters for rapid decompositions in condensed phases.

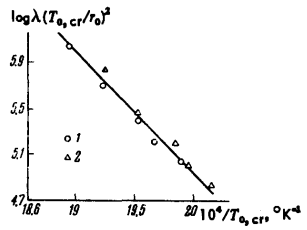

Fig.8. Critical thermal explosion condition for spherical particles of pyroxylin in a heated gas [52]: 1) air; 2) argon.

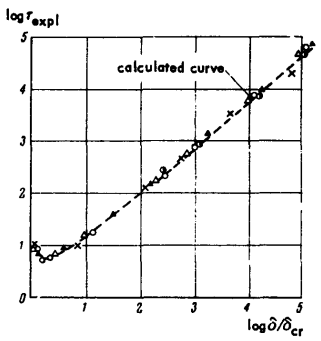

Fig. 9. Comparison of calculated (broken curve) and experimental values (points) of the time lag for the ignition of spherical particles of pyroxylin in a hot gas [52].

We shall not dwell on the other methods for the study of thermal explosions reported in the literature, because they lack proper theoretical foundations.

V. MECHANISM OF THERMAL EXPLOSION IN CONDENSED MEDIA

The very simple model of thermal explosion used as a basis for the classical theory can often be successfully applied to condensed systems. This is shown by the results of experimental investigations, some of which were discussed in the previous Section. However, thermal explosion in condensed media is, in general, a complex physicochemical reaction involving various phase transitions and associated effects in addition to chemical reaction.

We shall now briefly consider these physicochemical aspects of the mechanism of thermal explosions, and discuss the role of bulk gas evolution during thermal decomposition of a condensed material, of evaporation, of the formation of eutectics in the condensed phase, and of polymorphic transformations.

1. Effect of Bulk Gas Evolution during Decomposition on the Course of Thermal Explosion Processes

The role of bulk gas evolution depends on whether the process occurs in a solid or a liquid phase, whether it is fast or slow, and whether autocatalysis by gaseous decomposition products is possible.

One of the most interesting effects associated with gas evolution is convective heat transfer in liquid systems, resulting from the mixing effect of the bubbles of gaseous products on the reactant, and closely bound up with the rate of the chemical reaction.

The experimental work of Abramov and the present authors [64] on the critical thermal explosion conditions for molten tetryl has focussed attention on the specific features of thermal explosions in liquid media and on their relationship to the mechanism of stirring by gas bubbles. It was pointed out that:

1. The critical temperature $T_{0,cr}$ is strongly dependent on the material of the walls of the vessel: $T_{0,cr}$ is higher in a metal vessel than in a glass vessel.

2. The effective (overall) heat-transfer coefficient, calculated from the formula for the critical condition, increases with rise in temperature.

3. Pre-explosion heating-up is 3–5 times greater than the Semenov value:

$$\Delta T_{cr} = (3-5)\frac{RT_0^2}{E}.$$

4. The induction period at the thermal explosion limit is a much more sensitive function of temperature than the kinetic data suggest.

It should be stressed that this behaviour is shown by other liquids as well. In solids and gases, and also in liquids under conditions of rate limitation by external heat transfer, these observations do not apply. Merzhanov and coworkers [64] have given a qualitative explanation of these peculiarities in terms of stirring by bubbles.

Studies of the temperature field in a reacting liquid system at constant wall temperature are of considerable interest. The experimental results obtained by Barzykin and the present writers [75] indicate that in high-viscosity liquid systems the temperature profile does not differ appreciably from that in a solid (maximum heating-up at the centre and practically no heating-up close to the surface). In low-viscosity liquids a constant-temperature core appears in the reaction zone, and practically the whole of the thermal resistance of the system is concentrated in a thin boundary layer.

There is as yet no quantitative theory of thermal explosion in liquids which takes account of mixing effects, and the experimental results obtained under such conditions cannot be subjected to strict quantitative analysis. The most promising field for further studies is to acquire a fund of experimental data and to generalise it by simi-similarity methods, as is often done in the thoery of heat transfer.

Gaseous reaction products are frequently active, and capable of catalysing the reaction in progress. Under these conditions all the characteristics of the thermal explosion are strongly dependent on the conditions of removal of the gaseous products.

This dependence can be observed experimentally by controlling the escape of gaseous products through the pressure of the surrounding medium (constant-pressure bomb experiments). The most typical variation of the critical temperature $T_{0,cr}$ with pressure p is shown in Fig. 10 for a model mixture based on ammonium perchlorate (from

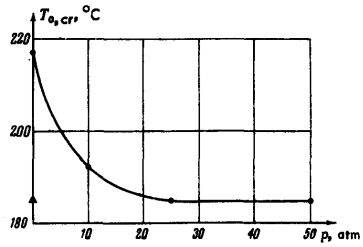

Fig. 10. Variation of critical temperature with pressure of inert gas. The solid triangle gives critical temperature in a sealed vessel without any free volume.

results obtained by Samoilenko, Abramov, and the present authors[75]). It is evident from the diagram that, as the pressure is increased, the critical temperature falls by ~ 30 deg, and thereafter stays constant. This lowering of the critical temperature occurs because the escape of gaseous reaction products is hindered by an increase in pressure, and this increases the catalytic effect of the products on the course of the reaction. The constancy of $T_{0,cr}$ at high pressures is probably due to the fact that at these pressures the gaseous products responsible for autocatalysis pass into the condensed state and cannot leave the reaction zone. It is significant that the value of $T_{0,cr}$ in the region of the plateau is the same as the value observed in a sealed vessel of the same diameter without any free volume. The gaseous reaction products cannot escape from the reaction zone in a sealed vessel, and the resulting complications are thus avoided. This is the simplest model for thermal explosions in a condensed phase: it will probably be widely applied in actual cases.

When discussing the thermal explosion of liquid explosives in open vessels, it is important to remember that the escape of gaseous reaction products produces a decrease in the reaction volume and alters its shape; this, in turn, affects both the formal kinetics of the thermal decomposition and the conditions of heat exchange between the reaction volume and the surroundings. The critical characteristics are altered because the volume occupied by the reacting system decreases a result of the escape of gaseous products, so that the concentration of the starting material and of the condensed products becomes higher than if the volume had remained unchanged. Thus, reaction velocities increase under conditions of changing volume. The conditions of heat exchange between the reaction volume and the external heat-transfer agent change because the ratio of the heat-emitting surface S to the volume of the condensed phase V is affected by the escape of gaseous products. We can distinguish two types of distortion of the model, simple shrinkage and frothing of the material. In the former case the behaviour of the system can be described mathematically[72], and expressions for the critical conditions and for the induction period of reactions of a specified type can be obtained. (These expressions are quite different from the corresponding expressions for the constant-volume case[44]). When frothing occurs the course of the reaction becomes more intermediate, and is fairly difficult to describe mathematically.

2. Thermal Explosion of Volatile Substances

The thermal explosion of substances which can evaporate has received very little attention. The literature of the 1930's and 1940's describes some experiments on the detonation of volatile substances, but the information given is inadequate for understanding the mechanism and developing a theory of the thermal explosion of volatile substances.

When analysing this phenomenon, it is important to remember that evaporation (or sublimation) in the presence of a chemical reaction in the bulk of the condensed phase, with evolution of gaseous products, follows quite a different course from evaporation in inert systems. Normally evaporation occurs from the surface of the material, and its rate is determined by the rate of diffusion of vapour in the gas phase above the surface and by the rate of supply of heat to the surface. In the case of a reacting system the rate of evaporation increases with the rate of gas evolution, because vapour is "entrained" by the mass flow of reaction products. Evaporation now becomes, as it were, a bulk process. Thus, when thermal decomposition and evaporation occur at the same time, an increase in the rate of the former process produces an increase in the rate of the latter. On the other hand, evaporation decreases the rate of the reaction, because: (1) evaporation consumes some of the starting material; (2) evaporation, being an endothermic process, absorbs a definite amount of heat. Evaporation occurring at the same time as thermal decomposition can therefore increase the induction period of the explosion and the critical temperature.

It should be noted that a given substance can behave, according to conditions, either as a volatile or as a non-volatile material. According to Belyaev[73], the determining factor is the relation between the temperature T_0, which characterises the reaction, and the boiling point T_b. If $T_0 > T_b$ or $T_0 \simeq T_b$, the evaporation is considerable, but if $T_0 \ll T_b$ the material behaves as though it were non-volatile. When $T_0 > T_b$ explosion cannot occur in the liquid phase, and the critical conditions are determined by reactions in a gas–vapour mixture.

3. Thermal Explosion of Organic Solids

Many solid organic explosives give rise to condensed decomposition products which form eutectic mixtures with the starting material. Eutectic formation, by converting some of the reactant into the liquid state, causes the reaction rate to increase, since the rate of decomposition of substances in the liquid state is higher than in the solid state.

A characteristic feature of these systems is autocatalysis of the reaction under isothermal conditions, arising from progressive dissolution of the starting material in the condensed reaction products. Solid-phase reaction is appreciable only in the initial stages of the decomposition; thereafter, the reaction occurs predominantly in the liquid phase.

On the assumption that the limiting step is associated with the kinetics of decomposition (and not with the kinetics of eutectic formation), i.e. that a state of quasi-equilibrium exists between the solid and the liquid phase, the kinetic features of the process can be put in mathematical form[74]. Unfortunately, the thermal explosion of

these materials (e.g. Hexogen and tetryl with T_0 below their melting points) has not been investigated experimentally, and there are no published data which illustrate the effects arising from eutectic formation.

4. Thermal Explosion in the Presence of Polymorphic Transformations

Polymorphic transformation (and, in general, any phase transition) affects the characteristics of thermal explosions in two ways: firstly, the transition to a new modification affects the laws governing the thermal decomposition and the thermophysical properties of the material, and secondly a definite quantity of heat is adsorbed (or evolved).

From the experimental results obtained by Abramov, Samoilenko, and the writers[75] for the thermal explosion of ammonium perchlorate, the development of thermal explosion in the presence of a polymorphic transformation shows the following pattern as a fuction of the relation between the experimental temperature T_0 and the phase transition temperature T_*:

1. $T_* < T_0$. The phase transition occurs during the heating-up stage, and its influence of the characteristics of the thermal explosion is not large.

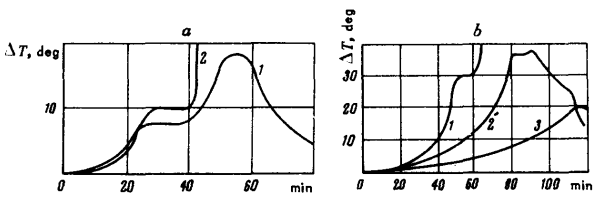

Fig. 11. Heating curves of ammonium perchlorate for different values of r (cm) and T_0:
a) 1) 1, 232°; 2) 1.25, 230°;
b) 1) 1.5, 212°; 2) 1.5, 206°; 3) 1.5, 202°.

2. $T_* - T_0 < RT_0^2/E$. The phase transition occurs during the pre-explosion period. The heat evolved in the reaction initially heats the material to T_*, and then is adsorbed by the phase transition. The critical conditions are determined, ultimately, by the reaction in the new phase (Fig. 11*a*).

3. $T_* - T_0 > RT_0^2/E$. The phase transition temperature is now reached during the substantially non-stationary régime; in this case the critical conditions are determined by the reaction in the old phase. It can happen, however, that the phase transition may halt the development of explosion: in this case the critical conditions are affected by the parameters of the phase transition (Fig. 11*b*), and the process is characterised by abnormally high pre-explosion heating-up.

A description of a process involving simultaneous chemical reaction and phase transition is of great theoretical interest, because the evolution of heat in the old phase makes methods of calculation based on Stefan's problem inapplicable.

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The theory of thermal explosions has undergone very important modification since it was first put forward. Present-day theory deals with a wide range of problems, differing in their physical content and practical importance. The development of the theory has been influenced by the overwhelming practical interest in condensed materials, which not only generated a number of specific problems but also brought about the solution of more general problems. Recent advances in computational techniques have contributed very significantly to the development of the theory. The solutions of the basic equations of thermal explosion in their general form, using numerical integration on fast electronic computers, has not only extended the computational equipment of the theory but also contributed to our understanding of the mechanism of the phenomenon. The theory of thermal explosions in its classical formulation has now been worked out in detail in its main aspects, and has been given a definitive form. More complicated thermal explosion régimes, particularly in the presence of physicochemical and hydrodynamic processes accompanying the chemical reaction, have not been adequately investigated, and their study is of the greatest interest in the further development of the theory of thermal explosions.

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FREE RADICALS AND CHEMILUMINESCENCE

V. Ya. Shlyapintokh

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I. INTRODUCTION

More than forty years ago, in the Laboratory of Electronic Chemistry of the Leningrad Physicotechnical Institute headed by Semenov, an investigation was begun of the mechanism and the kinetics of gas reactions, which subsequently resulted in a general theory of thermally explosive processes. New ideas on branching reactions, the possibility of isothermal chain explosions, on the effect of the dimensions of the reaction vessel and of additions of inert substances on the kinetics of chain reactions were developed on the basis of quantitative investigations of the oxidation of phosphorus vapour. It is interesting that the original aim of this work was not at all to investigate the kinetics of the process, but to study the effect of the oxygen pressure on the efficiency of the chemiluminescence accompanying oxidation. The impetus to make a kinetic study came from the discovery of peculiar and surprising critical phenomena. It was shown[1,2] that intense luminescence arises only within a definite range of oxygen pressures: at lower and higher pressures the reaction does not occur at all, and emission is absent. An experimental and theoretical analysis of this phenomenon by Semenov led to the formulation of the fundamental postulates of the theory of branched chain reactions. Thus it can be stated that a new stage in the development of kinetics and of several related fields of science began with investigations of chemiluminescence.

Although the oxidation of phosphorus was the first process explained in terms of the theory of branched chain reactions, the detailed mechanism of this process has hitherto been unknown, and the kinetic schemes which have been considered are hypothetical in character. Only the fact that the oxidation of phosphorus occurs by a radical-chain mechanism can be regarded as firmly established. It is therefore obvious that the chemiluminescence observed in this reaction is also due to the reactions of free radicals.

This conclusion, that chemiluminescence originates in the reactions of free radicals, applies not only to the oxidation of phosphorus. It applies generally to gas-phase reactions, and is firmly based on the pioneering quantitative investigations of chemiluminescence made by Polanyi, Kondrat'ev, Terenin, and their collaborators. Examination of the work of these and other authors on gas-phase systems shows that in all gas-phase chemical processes the occurrence of chemiluminescence is associated with the recombination (or disproportionation) of free radicals and atoms or with their addition to various species. The energy of these elementary acts is usually sufficient to produce electronically excited (or strongly vibrationally excited) species.

The principal laws of chemiluminescence were established on the basis of gas reactions. Its intensity was shown to be proportional to the rate of the elementary reaction in which excited species are formed. A quantitative study was made of the possible effect of secondary processes (quenching of excited states, transfer of energy) on the intensity of the emission. The investigations of chemiluminescence enabled quantitative information to be obtained on the relative and absolute concentrations of atoms and free radicals in flames and combustion products, on the rate constants of the reactions of these species, on the energy distribution of the products of elementary reactions, on the processes of energy exchange in collisions, on the bond energies in certain molecules, etc. The results of this work are quite well known, have been summarised in several reviews and monographs, and will not be considered in detail here. The purpose of the present review is to discuss the considerably less thoroughly studied question of the possibilities of using chemiluminescent methods in the quantitative investigation of the mechanism and the kinetics of radical and chain reactions occurring in the liquid phase. The possibilities of these methods have been demonstrated mainly in work on liquid-phase oxidation processes undertaken during recent years in the Institute of Chemical Physics of the USSR Academy of Sciences.

II. RELATION BETWEEN CHEMILUMINESCENCE AND MECHANISM OF THE OXIDATION OF ORGANIC SUBSTANCES BY MOLECULAR OXYGEN

It has recently been shown[3] that, in the liquid-phase oxidation of organic compounds by molecular oxygen, chemiluminescence arises in acts of disproportionation of peroxy-radicals. Therefore the intensity of emission in oxidation processes is characteristic not of the overall rate of the process but of the rate of interaction of peroxy-radicals, the intensity being proportional to the rate of this reaction.

In the simplest case, when a pure substance is undergoing oxidation with a fairly high oxygen concentration in the liquid phase, only one kind of radicals — peroxy-radicals of the oxidisable compound — is involved in the reaction. These radicals are formed either by reaction of the oxidisable substance with oxygen, as a result of thermal or catalytic dissociation of peroxy-compounds formed in the course of oxidation, or as a result of dissociation of specially added initiators. The radicals obtained take part in the chain reaction and are destroyed, thus exciting the luminescence.

In the steady state the rate of loss of radicals is equal to the rate of generation of chains. Hence in systems containing one species of free radicals, the intensity of the light is proportional to the rate of the process in which free radicals are formed, i.e. to the rate of initiation. The existence of this relationship enables chemiluminescence intensity measurements to be used as a rapid method for determining the kinetic characteristics of the initiation reaction (investigation of the mechanism of initiation, and determination of the activation energy, order, and rate constant of initiation, of number of radicals formed on the breakdown of one molecule of the initiator)[4-6].

Let us now examine a more complex system, containing two species — active and relatively inactive — of free radicals. Such a system can be obtained experimentally, for example, by adding an inhibitor to the oxidisable substance. In such a system one chemiluminescent reaction remains as before, since reactions of the inactive radicals (in this case inhibitor radicals) are insufficiently exothermic to excite chemiluminescence in the visible spectrum. Since some of the active peroxy-radicals are destroyed by interaction with the inhibitor, the rate of disproportionation of the peroxy-radicals does not equal their rate of formation, and the emission intensity I in such a system

measures not the rate of initiation but the concentration of peroxy-radicals RO_2, where $[RO_2] \propto \sqrt{I}$.

As the concentration of inhibitor interacting with the peroxy-radicals increases, the intensity of the emission diminishes. The concentration dependence of the emission intensity (with a constant rate of initiation) can be used[7-10] to measure the activities and concentrations of inhibitors, to determine the number of chains terminated by one molecule of inhibitor, to determine the rate of initiation, and also to investigate the mechanism of the inhibitor action.

If the reaction involves two species of active radicals, three chemiluminescent recombinations are possible in the system. Such a system can be obtained, for example, by adding a substance capable of reaction with the active radicals. One of the simplest systems containing two species of active radicals arises when small amounts of oxygen are introduced into a solution of an initiator in the oxidisable substance. Some of the alkyl radicals R present in the system are then converted by reaction with oxygen into RO_2. On the introduction of oxygen the intensity of the emission increases, since the oxygen-containing products of the recombination of the peroxy-radicals have emission bands in the visible part of the spectrum. Such bands are usually absent in the products of the recombination of R + R and R + RO_2 radicals. Therefore only one chemiluminescent reaction actually takes place in this system, and the emission intensity, as in the preceding case, measures the concentration of peroxy-radicals. The dependence of intensity on the concentration of dissolved oxygen in such a system can be used to estimate the relative reactivity of the alkyl radicals towards oxygen[11].

The quantum yield of chemiluminescence changes not only on passing from one type of radicals to another (e.g. from R to RO_2). It depends also on the structure of the radical R present in the free peroxy-radical. If peroxy-radicals of two kinds take part in the reaction (as e.g. in the co-oxidation of two compounds R^1H and R^2H), a change in the composition of the mixture is accompanied by a change in the relative concentrations of R^1O_2 and R^2O_2 radicals, and therefore the intensity of the emission depends on composition. When the chemiluminescence yields in simultaneous recombination reactions differ relatively little, the dependence of the intensity of emission on the concentration of one of the reactants is more complicated than in the preceding case. Under favourable conditions in such systems, however, it is possible to evaluate the kinetic parameters of the reaction from measurements of chemiluminescence[12].

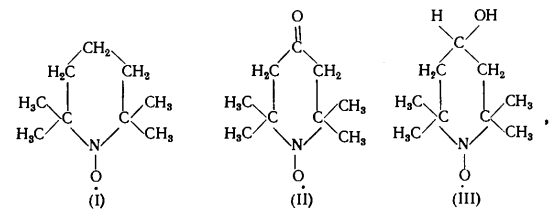
Thus quantitative studies of the laws of chemiluminescence in liquid-phase oxidations show that, in systems in which one chemiluminescent reaction occurs (or in systems in which the yield of chemiluminescence is much higher in one reaction than in the others), the emission intensity is a measure of the rate of recombination of free radicals. Therefore all factors which affect the concentration of radicals — temperature, reagent concentrations, additions of inhibitors, catalysts, etc. — influence the intensity of the luminescence. Furthermore, it is often possible from the emission intensity to follow the conversion of one kind of radicals into another. This opens up the possibility of determining from the emission intensity the relative concentration of free radicals and recording its variation both during the reaction and with change in the experimental conditions. In view of the great sensitivity of the chemiluminescent method, it is quite often the only direct method enabling changes in the concentration of free radicals to be recorded immediately.

III. USE OF CHEMILUMINESCENT METHODS TO INVESTIGATE THE MECHANISM OF THE ACTION OF ANTIOXIDANTS

In the present Section are discussed the results of several investigations in which the above ideas on the mechanism of chemiluminescence in inhibited oxidations have been used to elucidate the mechanism of the action of various inhibitors or antioxidants.

1. Mechanism of the Termination of Oxidation Chains by Stable Nitroxyl Radicals

Phenols and amines used as inhibitors form, on interaction with peroxy-radicals, unstable intermediate products, hydroperoxides, which readily break down to form free radicals, thus diminishing their effectiveness. Therefore great interest attaches to the search for inhibitors which terminate chains without forming branching agents. Among inhibitors of this type are the stable nitroxyl radicals



(I) (II) (III)

the mechanism of whose inhibiting action has been investigated[13].

Experiments were conducted with different concentrations of the nitroxyl radicals and different partial pressures of oxygen in the gaseous mixture bubbling through the oxidising ethylbenzene. During the experiments the concentrations of stable radicals were measured by the electron spin resonance method, and concentrations of peroxy-radicals by the chemiluminescent method. The experiments showed that, with sufficiently high oxygen concentrations, additions of stable radicals do not affect the intensity of the glow. Hence it follows that nitroxyl radicals R'NO· do not interact with the peroxy-radicals. They react vigorously, however, with alkyl radicals because, in the absence of oxygen, the nitroxyl radicals in concentrations exceeding 2×10^{-5} M are used up at the rate of initiation. Thus the inhibiting power of the nitroxyl radicals is determined by the relation between the rates of the two competing reactions

$$R + O_2 \xrightarrow{k_1} RO_2, \quad (1)$$

$$R + \dot{O}NR' \xrightarrow{k_2} \text{stable products.} \quad (2)$$

Fig. 1 shows how the emission intensity and the concentration of nitroxyl radicals (I) vary in the range of low oxygen concentrations when reactions (1) and (2) take place with comparable velocities. From these data the ratio of the kinetic constants $k_1/k_2 = 26 \pm 3$ for the nitroxyl radicals (I)–(III) was found. For the more stable alkyl radical of diphenylmethane this ratio is 1.4 ± 0.2, which can be explained by a lower value of k_1. Thus nitroxyl radicals can effectively suppress the oxidation chains of substances whose alkyl radicals are stabilised by conjugation and interact relatively slowly with oxygen, the effectiveness of the R'NO· radicals increasing as the oxygen concentration decreases.

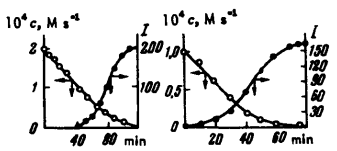


Fig. 1. Variation in concentration of nitroxyl radicals (I) and in intensity of chemiluminescence (in arbitrary units) at two initial concentrations of the nitroxyl radical (the nitrogen bubbling through ethylbenzene contains 9.3% of oxygen).

2. Interaction of the Hydroperoxide of Ethylbenzene with Benzenethiol in the Oxidation of Ethylbenzene

Available data [14-16] indicate that, in the oxidation of organic substances, compounds of the type of benzenethiol can react both with hydroperoxides and with peroxy-radicals. The occurrence of both reactions is readily detected from the kinetics of chemiluminescence [17]. The introduction of benzenethiol RSH into the oxidising ethylbenzene containing azoisobutyronitrile as initiator diminishes the emission intensity I. The dependence of I on [RSH] is of the same form as the corresponding relationship with other inhibitors, which do not react with the hydroperoxide, and it can be used to determine the rate constant for the reaction of benzenethiol with peroxy-radicals. Comparison with other inhibitors shows that benzenethiol reacts with peroxy-radicals just as effectively as does Ionol [4-methyl-2,6-di-t-butylphenol], which is frequently employed as an antioxidant.

Since benzenethiol acts as an inhibitor, it is gradually used up, and the emission intensity increases during the reaction. However, benzenethiol is consumed considerably more rapidly than is Ionol, which reacts solely with peroxy-radicals. This is seen formally from the fact that the mean number of chains terminated by one benzenethiol molecule is 0.3†, whereas Ionol terminates two chains. This difference can be explained by the additional benzenethiol required for reaction with the hydroperoxide. The latter reaction is detected from the chemiluminescence produced when benzenethiol is added to ethylbenzene containing hydroperoxide (~ 0.05 M). No emission is observed before the addition of benzenethiol, since the hydroperoxide dissociates too slowly under the experimental conditions. Additions of the inhibitor 1-naphthol weaken the resulting chemiluminescence. This implies that the hydroperoxide of ethylbenzene reacts with benzenethiol to form active radicals, which in ethylbenzene medium are converted into peroxy-radicals of ethylbenzene.

Thus an examination of the chemiluminescence shows that, in the initial stages of oxidation, when the hydroperoxide concentration is low, benzenethiol acts as an inhibitor. At later stages the additional reaction with hydroperoxide occurs.

3. Synergic Action of Inhibitors in the Oxidation of Hydrocarbons

Fig. 2*A* shows kinetic chemiluminescence curves representing the consumption of two inhibitors and of a mixture thereof in the oxidation of ethylbenzene initiated by azoisobutyronitrile [18]. It is seen that 1-naphthol (curve *1*) is a stronger inhibitor than is Neozone D [*N*-phenyl-2-naphthylamine] (curve *2*). At time $t = 0$, 1-naphthol — a lower concentration of which was taken — diminishes the emission intensity just as strongly as does Neozone D. Consequently the two inhibitors are initially consumed at the same rate. Since the concentration of 1-naphthol is one-fifth, its relative rate of consumption is the higher. With a mixture of the inhibitors in the same concentrations (curve *3*) the 1-naphthol is used up first, and then the Neozone D. This is seen from the shape of the curves.

Quite different behaviour (Fig. 2*B*) is shown by another pair, Neozone D (curve *1*) and the phenolic inhibitor Azolactone‡ (curve *2*). It is seen from Fig. 2*B* that, of these two inhibitors, Neozone D is the more active. With the mixture (curve *3*), however, the weaker phenolic inhibitor is used up first, and then the more active inhibitor. This corresponds to the gently sloping initial portion of the chemiluminescence curve, and at the later stages to the considerably steeper section, identical in shape with the chemiluminescence curve in the presence of pure Neozone D. Nevertheless, the emission intensities at time $t = 0$ for both inhibitor mixtures (Figs. 2*A* and 2*B*) agree well with the calculated values obtained from the known rate constants for the interaction of each inhibitor separately with peroxy-radicals [19]. Hence it follows that the inhibitors do not interact at the instant of mixing.

Investigations [18-22] combining the chemiluminescent methods described above with the usual methods of analysing the consumption of inhibitors during oxidation have enabled the synergic effect (Fig. 2*B*) to be explained by means of the reactions

$$\mathrm{AmH} + \mathrm{RO_2^{\cdot}} \rightarrow \mathrm{Am^{\cdot}} + \mathrm{ROOH}, \quad (3)$$

$$\mathrm{Am^{\cdot}} + \mathrm{PhOH} \rightarrow \mathrm{AmH} + \mathrm{PhO^{\cdot}}, \quad (4)$$

where AmH and Am· are respectively the amine and the free radical, and PhOH and PhO· the phenolic inhibitor and

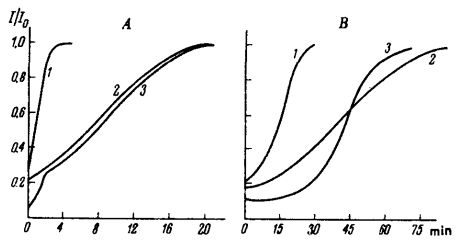


Fig. 2. Kinetic curves of chemiluminescence in the oxidation of ethylbenzene inhibited by additions of:
A): 1) 1-naphthol (0.22×10^{-5} M); 2) Neozone D (10^{-5} M); 3) a mixture of these inhibitors in the same concentrations;
B): 1) Neozone D (1.5×10^{-5} M); 2) the phenolic inhibitor Azolactone (4×10^{-5} M); 3) a mixture of these two inhibitors in the same concentrations.

† The number of chains terminated is determined from the kinetic chemiluminescence curves [10].

‡ 4-(4-Hydroxy-3,5-di-t-butylbenzylidene)-2-phenyloxazolone.

the resulting free radical. It follows from this scheme that the more active inhibitor — the amine — interacts with the peroxy-radicals, but is regenerated by reaction (4). As a result, the amine begins to be used up only after the weak, phenolic inhibitor has been consumed.

4. Mechanism of the Inhibiting Action of Phosphorous Esters

In order to elucidate the mechanism of the inhibiting action of phosphites, the kinetics of chemiluminescence has been investigated[23] in the oxidation of ethylbenzene, initiated by azoisobutyronitrile, in the presence of phosphites having various structures and of substances forming part of phosphite molecules. It has been shown, by the methods already described above, based on the weakening of chemiluminescence and on its kinetics, characterising the consumption of inhibitor, that only phosphites containing phenolic substituents possess high activity towards peroxy-radicals. Alkyl-substituted phosphites and phosphates, as well as phosphorous acid, hardly react at all with peroxy-radicals.

An interesting feature of the kinetic curves of chemiluminescence in the presence of phosphites containing phenolic substituents is that these compounds lower the emission intensity very little, and in this respect behave as weak inhibitors, while being at the same time very rapidly used up, like strong inhibitors, their rate of consumption exceeding by factors of 10–100 the rate of formation of radicals by dissociation of the initiator. If these compounds are stored not in a vacuum but in contact with the atmosphere, increase in the period of storage results in a gradual change in the character of the kinetic curves: the phosphites weaken the emission to an increasing extent, and their rate of consumption constantly decreases, approaching the rate of initiation. Hence it follows that the inhibiting power is possessed not by the phosphites themselves but by the phenols formed by hydrolysis of the former on storage. If a few per cent of a strong inhibitor is formed on hydrolysis, little weakening of the luminescence results, since the concentration of the added inhibitor is less than that of the phosphite by factors of several tens, and the calculated rates of consumption are far too high, since the calculation is based on the concentration of added phosphite.

This hypothetical mechanism is supported by an analysis of the emission curves in the presence of sufficiently high phosphite concentrations. Fig. 3 shows as example the emission curve for *o*-phenylene tri-t-butylphenyl phosphite. The curve contains two clearly marked sections *ab* and *bc*. The maximum slopes of these sections α agree precisely with the values α_1 for catechol (section *ab*) and α_2 for tri-t-butylphenol (*bc*), as shown by the broken straight lines. Thus the inhibiting action of phosphite in oxidation reactions is due to the reactions of their hydrolysis products.

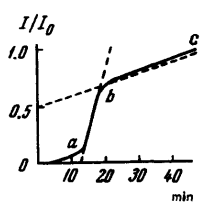


Fig. 3. Variation in relative intensity of chemiluminescence in the oxidation of ethylbenzene inhibited with added *o*-phenylene tri-t-butylphenyl phosphite.

IV. CHEMILUMINESCENT METHODS FOR MEASURING THE RATE CONSTANTS OF THE REACTIONS OF FREE RADICALS

Most methods for determining the rate constants for reactions of free radicals are based on measurements of non-stationary kinetics. Great difficulties are involved in determining kinetic constants by the direct measurement of steady-state concentrations of radicals. Slow chemical processes usually occur with low stationary radical concentrations, and only in rare cases is it possible to find a sufficiently sensitive method of measurement. The determination of the rate constants for reactions of free radicals is usually a complicated and laborious matter. The task is considerably simplified in several cases by the chemiluminescent methods which have appeared recently.

1. Chemiluminescent Method of the Photochemical After-effect

This method is based on measuring the kinetics of chemiluminescence in oxidation occurring under non-stationary conditions as a result of an abrupt change in the rate of initiation[24]. The time variation in the concentration of radicals under non-stationary conditions is described by the equation

$$\frac{d[RO_2]}{dt} = w_i - k_6[RO_2]^2, \qquad (5)$$

where w_i is the rate of initiation and k_6 the rate constant for recombination of the radicals. The form of solution of Eqn. (5) is determined by the initial conditions. If the photochemical reaction is conducted with a constant intensity of the exciting light, i.e. with constant w_i, a steady-state concentration of radicals

$$[RO_2]_{st} = \sqrt{\frac{w_i}{k_6}}, \qquad (6)$$

is established in the system.

After the light has been switched off, $w_i = 0$, and the concentration of radicals will fall as a result of their recombination:

$$-\frac{d[RO_2]}{dt} = k_6[RO_2]^2. \qquad (7)$$

The solution of Eqn. (7) is of the form

$$\frac{[RO_2]_{st}}{[RO_2]} - 1 = k_6[RO_2]_{st}t. \qquad (8)$$

Changing from radical concentrations to intensities, and making use of Eqn. (6), we obtain the expression

$$\sqrt{\frac{I_{st}}{I}} - 1 = \sqrt{k_5 w_i}\, t. \qquad (9)$$

which enables k_6 to be evaluated from the kinetics of the decay of chemiluminescence. Experimental determination of w_i in Eqn. (9) presents no difficulty, and can be effected in various ways.

The mean life of the radicals is

$$\tau = \frac{1}{\sqrt{w_i k_6}}. \quad (10)$$

The recombination rate constants of peroxy-radicals usually lie within the range 10^4–10^8 litres mole^{-1} s^{-1}. The high sensitivity of the chemiluminescent method enables experiments to be conducted at w_i of the order of 10^{-10} M × × s^{-1}. Under these conditions 10 s $\leq \tau \leq$ 1000 s, and the experimental measurement of the kinetics of chemiluminescence can be made with standard equipment using ordinary EPP-09 pen-recorders.

2. Chemiluminescent Method of the Oxygen Aftereffect

The oxygen aftereffect method[24-26], like that of the photochemical aftereffect, is used to determine recombination rate constants of the radicals from the kinetics of the establishment of a steady state recorded from the chemiluminescence. The difference consists in the method used to obtain a non-stationary concentration of radicals. In the oxygen aftereffect method, a non-stationary concentration of peroxy-radicals is produced by rapidly feeding oxygen to a system comprising a compound RH capable of oxidation and an initiator Y.

Before oxygen is admitted, the reactions

$$Y \rightarrow R' + R' + \text{products}, \quad (\text{rate of initiation } w_i)$$

$$R' + RH \rightarrow R'H + R,$$

$$R + R \rightarrow R_2,$$

take place in such a system, and the steady-state concentration of R radicals is

$$[R]_{st} = \sqrt{\frac{w_i}{k_4}}.$$

At the instant at which oxygen enters, the R radicals are converted very rapidly into RO_2 radicals by the reaction

$$R + O_2 \rightarrow RO_2, \quad (11)$$

the rate constant of which is so large that the change occurs in a very short time, and it can be assumed that the concentration of peroxy-radicals at the instant of entry of oxygen is $[RO_2]_0 = [R]_{st}$. Since the recombination rate constant of peroxy-radicals k_6 is in general different from the rate constant k_4, the initial concentration of the radicals $[RO_2]_0$ will be non-stationary. After the admission of oxygen and the conversion of R into RO_2 radicals, therefore, the concentration of the latter will begin to change, tending to the stationary value

$$[RO_2]_{st} = \sqrt{\frac{w_i}{k_6}}.$$

The kinetics of the variation in concentration of peroxy-radicals, and hence in the emission intensity, are described by the equations

$$\ln \frac{[RO_2]_{st} + [RO_2]}{[RO_2]_{st} - [RO_2]} \frac{[RO_2]_{st} - [RO_2]_0}{[RO_2]_{st} + [RO_2]_0} = 2\sqrt{w_i k_6}\, t, \quad (12)$$

$$\ln \frac{\sqrt{I_{st}} + \sqrt{I}}{\sqrt{I_{st}} - \sqrt{I}} \frac{\sqrt{I_{st}} - \sqrt{I_0}}{\sqrt{I_{st}} + \sqrt{I_0}} = 2\sqrt{w_i k_6}\, t, \quad (13)$$

obtained by solving Eqn. (5) with the condition $[RO_2] = [RO_2]_0$ at $t = 0$. The use of Eqn. (13) enables k_6 to be evaluated.

Since

$$k_4[R]^2_{st} = k_4[RO_2]^2_0 = k_6[RO_2]^2_{st} = w_i,$$

the value of k_6 thus obtained can be used to determine k_4:

$$k_4 = k_6 \frac{[RO_2]^2_{st}}{[RO_2]^2_0}$$

or

$$k_4 = k_6 \frac{I_{st}}{I_0}. \quad (14)$$

Thus the oxygen aftereffect method enables not only the recombination rate constant of peroxy-radicals k_6 (a process accompanied by luminescence) but also the rate constant for R radicals (recombination of which involves practically no emission) to be determined from a single experiment.

Fig. 4 shows possible kinetic curves for chemiluminescence with various relationships between the constants k_4 and k_6. Only when $k_4 = k_6$ (Fig. 4, curve *3*) does the oxygen aftereffect method become inapplicable.

The oxygen aftereffect has been measured[24] in the oxidation of cumene and of ethylbenzene. The measurements show that for cumene $k_4 \gg k_6$, as can be seen from the absence of an initial jump in intensity in the kinetics of the chemiluminescence (Fig. 5). In this case it can be assumed that $[RO_2]_0 = 0$, and the kinetics can be described by Eqn. (13) in the form

$$\ln \frac{\sqrt{I_{st}} + \sqrt{I}}{\sqrt{I_{st}} - \sqrt{I}} = 2\sqrt{k_6 w_i}\, t. \quad (15)$$

This equation reproduces the experimental relationship well (Fig. 5). The value obtained for k_6 agrees well with the value determined by the classical method of intermittent illumination[27].

Kinetic curves of the type of curve *2* in Fig. 4 were obtained for ethylbenzene (Fig. 5), and from them recombination rate constants of 4×10^7 (k_6) and 2×10^8 litres mole^{-1} × × s^{-1} were obtained for peroxy-radicals and hydrocarbon radicals respectively.

The oxygen aftereffect method has been employed[28] to investigate the effect of the solvent — glacial acetic acid — on the recombination rate constant k_6 of peroxy-radicals from cumene. It was found that k_6 increases with increase in the acid concentration, being approximately doubled on passing from pure cumene to a 30% solution of cumene in the acid,

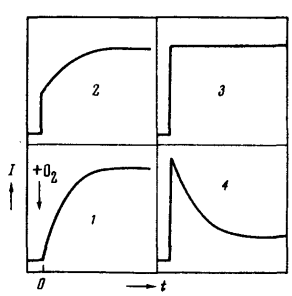


Fig. 4. Diagrammatic kinetic curves of chemiluminescence:
1) $k_4 \gg k_6$; 2) $k_4 > k_6$; 3) $k_4 = k_6$; 4) $k_4 < k_6$.

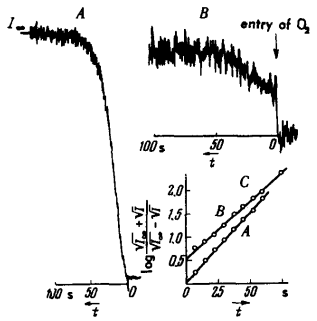


Fig. 5. Kinetics of chemiluminescence after rapid saturation with oxygen:
A) cumene, with dicyclohexyl peroxodicarbonate as initiator at 40° with $w_i = 1.49 \times \times 10^{-8}$ M s^{-1}; *B*) ethylbenzene with azoethylbenzene as initiator at 36° with $w_i = 1.75 \times \times 10^{-8}$ M s^{-1}; *C*) anamorphoses of curves *A* and *B*.

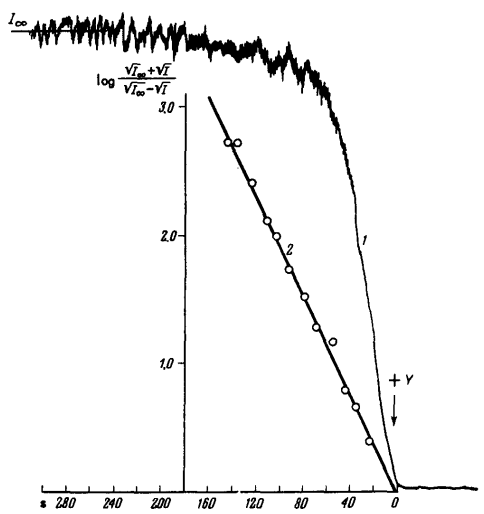


Fig. 6. Kinetics of chemiluminescence *I* after introduction of initiator Y (at instant indicated by arrow) into a solution of butan-2-one in benzene (1 : 4) with $w_i = 3.8 \times 10^{-8}$ M s^{-1} at 60°:
1) kinetic curve; 2) semi-logarithmic anamorphosis of curve 1.

while the rate constant of chain propagation remains practically unchanged. As a result of the increase in k_6, the rate of oxidation of cumene in the 30% solution falls by one-third (with the effect of dilution taken into account).

3. Chemiluminescent Method of Rapid Heating

Apart from the methods already described for producing non-stationary conditions in order to determine the rate constants of radical reactions from the kinetics of chemiluminescence, we can use rapid heating, addition of some reagent (initiator, oxidisable substance, inhibitor, etc.), cessation or change in intensity of initiation accomplished by means of ultrasonic vibrations, penetrating radiation, an electrode reaction, etc. Only some of these methods have hitherto been used in measuring rate constants. Thus the heating method has been used[29-31] in estimating the recombination rate constant for radicals of the initiator azoisobutyronitrile. The method involves adding a small volume (~ 0.1–0.01 ml) of the initiator to a heated inert solvent — chlorobenzene (containing an activator — a substance which intensifies the emission — and oxygen) — and recording the kinetic chemiluminescence curve, which reflects the kinetics of the accumulation of initiator radicals. At the instant of addition of the initiator $[RO_2]_0 = 0$, $I = 0$, and the kinetics of chemiluminescence is described by Eqn. (15).

According to these estimates $3 \times 10^7 < k_6 < 9 \times 10^7$ litres $\times \times$ mole^{-1} s^{-1};[29] a value of $(1.6 \pm 0.8) \times 10^8$ litres mole^{-1} s^{-1} has been given in Ref. 31.

The heating method has been used[32] to investigate the effect of the medium on the recombination rate constant of the peroxy-radicals of butan-2-one. The difference from the work just mentioned consisted in adding a small volume of initiator solution not to a heated inert solvent but to the oxidisable substance (butan-2-one) or to a mixture of the latter and some solvent (benzene, water, nitrobenzene). The kinetics of chemiluminescence in this system is also described by Eqn. (15), which, as can be seen from Fig. 6, is well satisfied.

It was shown[32] that additions of benzene and water produce a decrease in the values of k_6, whereas additions of nitrobenzene produce an increase. The effects are quite marked: addition of 20 mole % of benzene more than halves k_6, and of water diminishes it almost to one-quarter whereas this addition of nitrobenzene produces a sevenfold increase in k_6.

It may be remarked that Refs. 28 and 32 report the first investigations of the effect of a solvent on the rate constants of the elementary reactions of free radicals in oxidation processes. Such studies have not previously been made, since the measurement even of one value of a constant was extremely time-consuming.

V. CHEMILUMINESCENCE OF IRRADIATED PROTEINS, NUCLEIC ACIDS, AND SYNTHETIC POLYMERS

Research papers have recently appeared on the chemiluminescence of irradiated proteins, nucleic acids, and synthetic polymers, which have established a link between free-radical processes and chemiluminescence. Chemiluminescent methods have been employed in this work to identify free radicals, determine the kinetics of radical destruction, reveal the reactions leading to the formation of free radicals, and assess the protective effect against radiation of compounds of various classes.

Chemiluminescence has been detected[33-35] in dry irradiated synthetic polymers and biopolymers, such as poly(methyl methacrylate), polystyrene, bovine serum albumin, human serum albumin, egg albumin, casein, etc. Comparison of the curves for the decay in chemiluminescence and for the fall in concentration of free radicals after irradiation (radical concentrations measured by the electron spin resonance method) showed that the chemiluminescence curves represent quantitatively the fall in radical

concentration. If the emission and radical-concentration curves are superposed at one point by changing the scale of the vertical axis, the curves coincide completely. This permits the chemiluminescent method to be used to investigate the kinetics of radical destruction at small radiation doses, when the sensitivity of the electron spin resonance spectrometer is inadequate.

Similar relationships have been obtained in studying the flash of chemiluminescence accompanying the dissolution of irradiated proteins and polymers[35]. Fig. 7 shows the kinetic curves for emission (full line) and radical concentration (points) in the dissolution of irradiated poly(methyl methacrylate) in dichloroethane. It is seen from Fig. 7 that in this case, too, the time variation of the emission reproduces the kinetics of the loss of radicals.

The luminescence becomes weaker or completely disappears when oxygen is removed. Addition to the solution of inhibitors for free-radical processes (e.g. Ionol) results in a diminished intensity of emission.

It was shown in the above papers that luminescence was associated with the recombination of peroxy-radicals. The coincidence of the kinetic curves for emission and loss of radicals was explained by limitation of the kinetics by processes of dissolution and diffusion of oxygen in the solvent. In view of the complexity of the systems, the experimental results do not yet provide, in the absence of many postulates, quantitative information on the elementary processes of the addition of oxygen or on the recombination rate constants of the radicals.

The investigation of the reactions of free radicals in solution is of special interest to radiation biology. Chemiluminescent methods can also be used in this work. Employment of a highly sensitive flow-type apparatus[36] has enabled a prolonged afterglow to be recorded in aqueous solutions of certain proteins and polymers — serum albumin, haemoglobin, trypsin, poly(ethylene oxide), polyvinylpyrrolidone, etc. — which have been irradiated with small doses of ultraviolet radiation and X-rays[37,38]. The investigation led to the conclusion that the afterglow represented chemiluminescence accompanying the recombination of peroxy-radicals[38].

Investigation of the effect of various substances on the kinetics of the afterglow has shown[39,40] that the rate of extinction of the light is most strongly increased by substances which possess a protective action against radiation (those containing sulphur, phenols). These substances

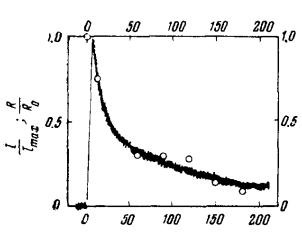


Fig. 7. Kinetics of the variation in the relative intensity of chemiluminescence (full curve) and kinetics of variation in relative concentration of radicals (points on curve) in the dissolution of irradiated poly(methyl methacrylate) in 1,2-dichloroethane.

influence the kinetics still more strongly if they are introduced into the system before exposure. Substances with feebly developed radiation-protective properties, however, exert little influence on the kinetics of the afterglow. Further investigation of the mechanism of the long-lived afterglow will probably help to elucidate several aspects of the primary action of radiation. Determination of the kinetics of the afterglow may also prove useful for a preliminary selection of radiation-protective substances.

A study has been made[41,42] of the afterglow in aqueous solutions of deoxyribonucleic acids (DNA) which have been irradiated at room temperature. Chemiluminescence was observed when the solutions were heated above 40°. The luminescence was shown to be associated with the breakdown of unstable peroxy-compounds of the DNA, formed during irradiation in the presence of oxygen. The kinetics of the decay of the emission, representing the rate of decomposition of the initiator, was used to evaluate the decomposition rate constants of the peroxy-compounds and the activation energy (13 kcal mole^{-1}). This value is identical with the activation energy for breakdown of the least stable DNA hydroperoxide and cytosine hydroperoxide[42]. The initial emission intensity is proportional to the concentration of peroxy-compounds of the DNA, and this relationship can be used to determine the content of peroxy-compounds in the irradiated solutions. Chemiluminescence in these systems is obviously associated with the reactions of free radicals, as is indicated by the weakening of the glow produced by antioxidants. Those inhibitors (e.g. propyl gallate) which considerably diminish the postradiation fall in viscosity of DNA solutions are most effective in diminishing the intensity of the chemiluminescence of DNA. When inhibitors which have a feeble effect on the postradiation fall in viscosity are added after irradiation, the emission intensity also changes insignificantly. These results again show the possibility of employing chemiluminescent methods to assess the radiation-protective effects of different compounds.

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In recent years, evidence has accumulated in favour of the possibility of free-radical formation by a bimolecular reaction between valency-saturated molecules:

$$R'X + YR'' \rightarrow R'\cdot + XY + R''\cdot, \quad (1)$$

In 1954, Semenov[1] published the first theoretical discussion, in a general form, of the kinetic features of reactions of this type, and arrived at the seemingly paradoxical conclusion that their activation-energy barrier should be relatively small.

This conclusion was reached on applying the principle of detailed equilibrium to certain reactions of atoms and radicals. Thus, we know[2] that the disproportionation of free ethyl radicals occurs with a very low activation energy. Hence it is a thermodynamic necessity that the reverse reaction (formation of two ethyl radicals from a molecule of ethylene and one of ethane) should also be attended by a negligible activation barrier[3], and that its activation energy should be fully accounted for by the endothermicity of the process (~ 60 kcal mole^{-1}).

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This conclusion was reached on applying the principle of detailed equilibrium to certain reactions of atoms and radicals. Thus, we know[2] that the disproportionation of free ethyl radicals occurs with a very low activation energy. Hence it is a thermodynamic necessity that the reverse reaction (formation of two ethyl radicals from a molecule of ethylene and one of ethane) should also be attended by a negligible activation barrier[3], and that its activation energy should be fully accounted for by the endothermicity of the process (~ 60 kcal mole^{-1}).

A qualitative discussion of the activation energy of the reaction

$$H_2 + Cl_2 \rightarrow H\cdot + HCl + Cl\cdot, \qquad (2)$$

starting from the reverse reaction between the two atoms ($H^{\cdot}$ and $Cl^{\cdot}$) and a molecule of hydrogen chloride, leads to the same conclusion.

Arguing that a termolecular reaction between two atoms and a molecule should involve a low activation barrier, Semenov concluded that the activation energy of the bimolecular reaction (2) must be largely determined by the endothermicity of this reaction.

These ideas were confirmed in Semenov's book [1] by an approximate quantum-mechanical calculation of the activation energy of the reaction

$$H_2 + H_2 \rightarrow H\cdot + H_2 + H\cdot, \qquad (3)$$

using London's method.

The activation barrier to reaction (3), on the assumption of a linear configuration of the atoms in the transition complex, turned out to be lower than the activation energy of the reaction

$$H\cdot + H_2 \rightarrow H_2 + H\cdot.$$

Griffing's molecular orbital calculation [4,5] of the activation energy of reaction (3) confirmed that the activation barrier is small when the hydrogen atoms in the transition complex are arranged in a straight line.

In 1958 Semenov discussed [1] from a general standpoint the experimental data then available on reactions proceeding according to scheme (1) and also according to scheme (1'),

$$RX + \rangle C{=}C\langle \rightarrow R\cdot + X{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot, \qquad (1')$$

which is a particular case of scheme (1). He showed that many baffling results could be simply explained in terms of the proposed mechanism.

By studying reactions of this type, it was possible to envisage systems in which the formation of radicals would be most likely to follow scheme (1) or scheme (1').

Subsequent researches into reactions of this type have been carried out much more systematically, mainly at the Institute of Chemical Physics of the USSR Academy of Sciences. The present Review deals primarily with the experimental results obtained since the publication of Semenov's book [1] in 1958, with particular emphasis on kinetic investigations.

II. GENERAL CONSIDERATIONS

The reaction between two molecules R'X and R''Y with formation of two radicals according to scheme (1) is in most cases endothermic, because two covalent bonds are broken (R'–X and R''–Y) but only one new bond is formed (X–Y). If, in accordance with Semenov's views, the activation energy of reactions of this type is largely determined by the heat absorbed (in other words, if the activation barrier is small), the reaction will actually take place when D(X–Y) $\gg D$(R'–X) and D(X–Y) $\gg D$(R''–Y), and the heat of reaction (1), $q = D$(X–Y) - D(R'–X) - D(R''–Y), will not be much less than zero.

It can be shown that this condition is satisfied if the bond formed by the reaction is appreciably more polar than the two broken bonds. Thus, using Pauling's postulate of the additivity of normal covalent bond energies, we find that

$$D(R' - X) = \frac{D(R' - R') + D(X - X)}{2} + \Delta_{R'X},$$

$$D(R'' - Y) = \frac{D(R'' - R'') + D(Y - Y)}{2} + \Delta_{R''Y},$$

$$D(X - Y) = \frac{D(X - X) + D(Y - Y)}{2} + \Delta_{XY},$$

where $\Delta_{R'X}$, $\Delta_{R''Y}$, and Δ_{XY} are the departures from covalency of the bonds in the particular molecules.

Thus,

$$q = -\frac{D(R' - R') + D(R'' - R'')}{2} + \Delta_{XY} - \Delta_{R'X} - \Delta_{R''Y} =$$

$$= -\quad (R' - R'') + \Delta_{XY} - \Delta_{R'X} - \Delta_{R''Y} + \Delta_{R'R''}, \qquad (I)$$

where D(R'–R'') and $\Delta_{R'R''}$ are the bond energy and the departure of the bond from covalency in the molecule R'R''.

It follows from formula (I) that, if the bonds which are broken and formed in the reaction are non-polar, the heat of the reaction is equal to the energy of the R'–R'' bond, and is therefore of the order of tens of kilocalories per mole.

In order to make reaction (1) less endothermic (for a given R'–R'' bond), the departure from covalency Δ_{XY} must considerably exceed the sum $\Delta_{R'X} + \Delta_{R''Y}$. For the particular case of reaction (1)

$$X_2 + Y_2 \rightarrow X\cdot + XY + Y\cdot,$$

where the bonds in the original molecules are, of course, non-polar, formula (I) reduces to

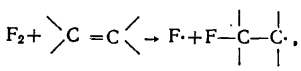
$$q = -D(X - Y) + 2\Delta_{XY}. \qquad (II)$$

We conclude from formulae (I) and (II) that a reaction of the type (1) becomes thermodynamically possible and kinetically real if one of the reactants is strongly oxidising or strongly reducing with respect to the other, so that the atom X in the resulting compound XY transfers an electron to Y (or conversely attracts an electron from the electron cloud of Y) thus making Δ_{XY} large. It follows that reaction (1) will occur in practice if it is a typical oxidation–reduction interaction. Not surprisingly, therefore, known cases of this reaction involve strong oxidising or reducing agents, e.g. oxygen, halogens, and peroxides with saturated and unsaturated hydrocarbons, peroxides with amines and sulphides, organometallic compounds with alkyl halides, etc. On the other hand, it should be noted that scheme (1) does not cover all possible cases of radical formation in redox systems [6-12].

As stated above, application of the principle of detailed equilibrium predicts an activation energy equal to the heat of reaction for strongly endothermic reactions giving rise to atoms and radicals: in other words, the activation barrier is vanishingly small. Furthermore, the theory predicts a linear configuration of the atoms in the transition complex for reactions between two H_2 molecules. This conclusion has been confirmed by quantum-mechanical calculations [1,4].

When extending these conclusions to other systems of more practical importance, we should not expect a linear

activated complex in all cases. Thus, a non-linear structure will probably be more favourable if not only s electrons are involved in the formation of bonds in the transition complex. For example, in the reaction between olefins and halogens



the most favourable configuration of the transition complex is probably one in which the F–F and C–C bonds are mutually almost perpendicular.

Not even the conclusion of a zero activation barrier can be assumed to apply unequivocally to all real systems. Thus, although the overall activation energy E (including the heat of reaction q) decreases on going from strongly exothermic towards thermally neutral processes, there is no reason to suppose that E tends to zero for thermally neutral reactions, i.e. that when $q = 0$ the activation barrier $\epsilon = E - q$ is zero.

The approximate Polanyi–Semenov relation [1]

$$\varepsilon = A - \alpha q, \qquad \text{(III)}$$

is known to hold for free-radical reactions: in other words, ϵ is a maximum for $q = 0$.

Semenov has given evidence [1] showing that expression (III) is generally applicable to the kinetics of elementary reactions and is by no means confined to reactions between radicals and molecules. When the transition complex has a complicated structure, the quantity A, which depends on many factors, such as bond elongation, distortion of valence angles, etc., does not remain constant even in series of related reactions. This introduces a deviation from linearity in the relation between ϵ and q.

The reactions represented by scheme (1) are similar to radical reactions in the simplicity of structure of the transition complex, since in both cases the valence angles are not significantly distorted on formation of the transition complex. We can therefore expect expression (III) to hold, with constant values of A and α, in series of related reactions of this type. Thus, the activation barrier will evidently not be zero, and will be a maximum for thermally neutral reactions.

III. THE STERIC FACTOR IN BIMOLECULAR REACTIONS INVOLVING VALENCY-SATURATED MOLECULES

Table 1 lists the preexponential factors of a number of reactions, calculated by the transition state method. In most cases, the transition complex was assumed to have a linear configuration. As was to be expected, the steric factor P is in many cases much less than unity. For the relatively simple molecules considered in Table 1, and for reactions between a diatomic molecule and a complicated molecule, P lies in the range 10^{-1}–10^{-5}.

TABLE 1.

Reaction	$10^{-10}A$, $cm^3\ s^{-1}$
$H_2+C_2H_5 \rightarrow H+C_2H_6$	3.32 [24]
$H_2+H_2 \rightarrow H\cdots H\cdots H \rightarrow H+H_2+H$	4670
$F_2+H_2 \rightarrow F\cdots F\cdots H\cdots H \rightarrow F+HF+H$	530
$F_2+HBr \rightarrow F\cdots F\cdots H\cdots Br \rightarrow F+HF+Br$	7.80
$F_2+HI \rightarrow F\cdots F\cdots H\cdots I \rightarrow F+HF+I$	6.26

IV. SPECIFIC SYSTEMS

1. Reactions of Molecular Oxygen

The bimolecular reaction

$$RH + O_2 \rightarrow R\cdot + HO_2\cdot, \qquad (4)$$

is a well-known example of initiation of oxidation, and of some other chain reactions [1,13].

Nalbandyan and his coworkers [14] have recently studied this reaction in the particular case of acetaldehyde. They found that hydrogen peroxide is a primary product of the molecular reaction, which suggests the mechanism

$$CH_3C(=O)H + O_2 \rightarrow CH_3\dot{C}O + HO_2\cdot, \qquad (5)$$
$$HO_2\cdot + CH_3COH \rightarrow H_2O_2 + CH_3\dot{C}O.$$

In agreement with earlier data [15,16], the activation energy of the reaction was found to be 30 kcal mole^{-1}, which is not very different from the heat of reaction (5).

Extending Semenov's approach to liquid-phase oxidation, Denisov showed [17–19] that free radicals can be formed in the termolecular reaction between RH and oxygen

$$RH + O_2 + HR \rightarrow R\cdot + H_2O_2 + R\cdot.$$

When $D(R–H) < 90$ kcal mole^{-1} the termolecular reaction is less endothermic than the bimolecular reaction (4). Assuming that the activation energy was fully accounted for by the heat of reaction, Denisov concluded that at high hydrocarbon concentrations (10 M) the termolecular reaction should be faster than the bimolecular reaction for hydrocarbons and other compounds having a bond energy $D(R–H) < 90$ kcal mole^{-1}.

Experimental results for a number of compounds have confirmed the formation of radicals by a termolecular mechanism [18–21]. These results, and those of other authors, are summarised in a review [19] and in a monograph [13].

2. Reactions of Peroxides

The decomposition of the hydroperoxides formed as intermediates in oxidations is a reaction of the type known as "degenerate chain branching". It is now realised that, in addition to the unimolecular decomposition ROOH → → RO$^{\cdot}$ + $^{\cdot}$OH, the bimolecular reactions of hydroperoxide molecules with the following species are very important sources of free radicals

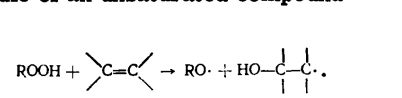
(a) another molecule of the hydroperoxide [22]

$$2\,ROOH \rightarrow RO\cdot + H_2O + ROO\cdot.$$

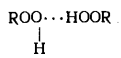
(b) a solvent molecule [1,23,24]

$$ROOH + R'H \rightarrow RO\cdot + H_2O + R'\cdot.$$

(c) a molecule of an unsaturated compound [19]



A hydrogen-bonded intermediate association complex[22] could be a precursor in the bimolecular interaction of two hydroperoxide molecules:



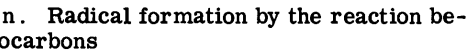
We can envisage two extreme cases, leading to entirely different reaction kinetics. If the equilibrium lies far over towards the monomeric hydroperoxide molecules, it is easy to see that both the kinetic equation and the reaction rate will be indistinguishable from those corresponding to the bimolecular reaction between two hydroperoxide molecules. In other cases, the concentration of the association complex may be the predominant factor, and in this case the reaction will occur through this complex and follow first-order kinetics.

More detailed experimental results on the formation of radicals from hydroperoxides can be found in the reviews mentioned above[13,19].

3. Reactions of Molecular Fluorine

(*a*) Initiation. Radical formation by the reaction between F_2 and hydrocarbons

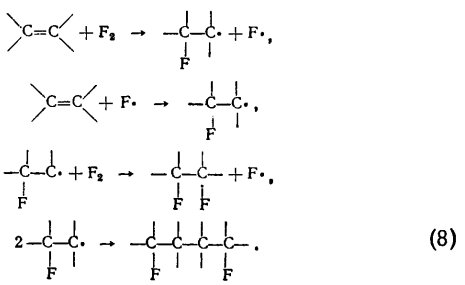
(6)



(7)

is particularly favourable thermodynamically, because all reactions of these two types are either practically athermic or exothermic. Miller[25-27], as long ago as 1956, pointed out that these reactions have to be included in the fluorination scheme in order to explain the reaction products, particularly in the case of olefins.

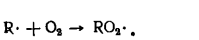
As a result of his study of the fluorination products of olefins over a range of temperatures, Miller proposes the following scheme for the reaction between F_2 and olefins[28]



(8)

The high rate of formation of radicals explains the relatively high yield (tens per cent) of the dimeric product in reaction (8).

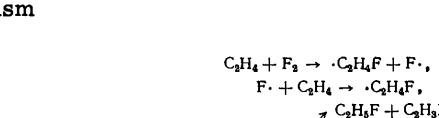
A direct confirmation of the formation of radicals during the reaction between F_2 and olefins was obtained by Kapralova and Shilov[29], who studied these reactions by the electron spin resonance method. They found that, when fluorine is passed over an olefin frozen at the temperature of liquid nitrogen, free radicals are formed on the surface. These radicals were shown to be peroxidic and to result from the interaction of the primary radicals with oxygen, present as an impurity in the fluorine:



According to their rate of reaction with fluorine when frozen at 77°K, ethylene and its derivatives can be arranged in the sequence[30]

The first three members of the series react too fast for accurate measurement even at liquid nitrogen temperature. The temperature at which these reactions take place indicates that the activation energy must be low: the experimental value for the reaction between F_2 and C_2HCl_3 is close to 0.5 kcal mole^{-1}

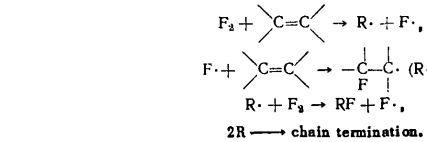
The elementary reaction between fluorine and ethylene has been investigated in the gas phase by the low-pressure flame method[30,31]. The conditions (very large excess of ethylene) are chosen so as to exclude secondary chain propagation reactions ($R^{\cdot} + F_2 \rightarrow RF + F^{\cdot}$) when the rate constant of the primary reaction between F_2 and C_2H_4 is large. The products of the reaction were identified as C_2H_3F, C_2H_5F, and $C_4H_8F_2$, corresponding to the mechanism



(9)

The absence of $C_2H_4F_2$ among the reaction products shows that chain propagation is effectively excluded under the chosen conditions. The rate constant of reaction (9) is $8 \times 10^{14} \exp(-4600/RT)$ cm^3 s^{-1}.

Rodgers[32,33] studied the kinetics of the slow gas-phase reactions of fluorine with 2,3-dichlorohexafluorobut-2-ene and with perfluorobut-2-ene. His kinetic results are consistent with the following chain mechanism for the fluorination:



(7)

From the overall activation energy for the reaction Rodgers, estimated the activation energy for reaction (7), assuming values close to zero for the other reactions. The activation energy of the chain generation reaction was found to be quite large — 16 kcal mole^{-1} for perfluorobutene and 23–25 kcal mole^{-1} for dichlorohexafluorobutene.

Thus, the activation energy of reactions of type (7) is not zero, even for ethylene, whose reaction is exothermic by 16 kcal. When electronegative substituents are introduced into the olefin molecule, the activation energy increases for surface and gas-phase reactions alike. This may be partly caused by a decrease in the enthalpy change accompanying the elementary reaction of fluorine with the olefins, but the available experimental data do not allow us to establish a quantitative relationship. There is a substantial difference in activation energy between the gas-phase reactions of fluorine and the surface reactions, the latter having the lower value of ϵ. This is evidently a manifestation of the specificity of surface reactions, in which the resulting free radical remains bound to the surface.

Very much less is known about elementary reactions of fluorine of the type

$$RH + F_2 \rightarrow R\cdot + HF + F\cdot.$$

The only reaction of this type which has been the object of a kinetic study is the reaction

$$F_2 + HI \rightarrow F\cdot + FH + I\cdot. \quad (10)$$

This reaction was investigated by the low-pressure flame method[30]: the measured activation energy was 3.5 kcal mole^{-1}. However, it is possible that the authors failed to exclude the chain reaction completely, and that the true activation energy is somewhat higher.

Reaction (10) is unique in the value of its heat of reaction. In other cases, e.g.

$$F_2 + H_2 \rightarrow F\cdot + FH + H\cdot, \quad (11)$$

$$F_2 + HCl \rightarrow F\cdot + FH + Cl\cdot, \quad (12)$$

$$F_2 + CH_4 \rightarrow F\cdot + FH + CH_3\cdot, \quad (13)$$

$$F_2 + C_4H_{10} \rightarrow F\cdot + FH + C_4H_9\cdot, \quad (14)$$

the thermal effect is much smaller. The rate constants and activation energies of these reactions are not known. Several workers[30,34-36] have shown that under certain conditions the fluorination of hydrogen, hydrogen chloride, methane, and butane is very slow or even undetectable at room temperature or above. Under different conditions the fluorination of those same compounds is known to proceed explosively by a spontaneous thermal or chain reaction[37]. A high reaction rate is not sufficient proof that the elementary reactions (11)–(14) occur readily, since the rate of initiation may not play an essential role. On the other hand, the fact that under certain conditions the fluorination is immeasurably slow proves that the rate constant of the elementary reactions (11)–(14) is small and that their activation energy is large.

Published experimental results[30,34-36] in conjunction with the data of Table 1 enable us to estimate a lower limit for the activation energy of these reactions: the value thus obtained is ~ 15–20 kcal mole^{-1}. In fact, the activation energy can, of course, be as much higher as we wish. This is evidence for the existence of a considerable activation barrier in practically athermic reactions of fluorine, proceeding according to scheme (6).

(*b*) Chain Branching. We have already pointed out that the bimolecular reaction of hydroperoxides with various compounds can provide a chain-branching mechanism in chain reactions in which hydroperoxides are formed as intermediates. Reaction (4) can also act as a branching process if RH is an intermediate product and the bond energy D(R–H) is much lower than in the original compound. Branching of this type occurs, for example, in the high-temperature oxidation of methane. In this case the branching product is formaldehyde, which reacts with O_2 according to scheme (4). From the point of view of reaction mechanism, this so-called "degenerate" branching is indistinguishable from initiation. Thus, a degenerate branching reaction is either a unimolecular decomposition or a bimolecular reaction involving a molecule of an intermediate product which is chemically more reactive than the starting compound.

Somewhat similar ideas have been developed[37] in recent years for the non-degenerate branching mechanism, which causes spontaneous ignition by a chain reaction. It has been shown[38-40] that the reactions of molecular fluorine involve a branching chain mechanism, the branching of the chains being realised by chemical reactions of intermediate species.

The difference from degenerate branching resides in the fact that the intermediate species react in an excited state, for which the excitation energy is supplied by exothermic chain development reactions. Thus, the concentration of these intermediate species does not follow the Maxwell–Boltzmann energy distribution. The life of the excited particles, limited by energy dissipation by collisions, is short and of the same order as the time of chain development. If the particle is able to react during this time with formation of atoms or radicals, chain branching occurs. The branching can proceed either as a unimolecular decomposition at the weakest bond or as a bimolecular chemical reaction between excited particles and the initial molecules.

The chain branching which occurs during fluorination of hydrogen[40] is an example of a bimolecular branching reaction. It has been shown that this reaction has definite pressure limits, separating a region of extremely slow reaction from a region of spontaneous ignition. In view of the relative simplicity of the system $H_2 + F_2$, we can unambiguously identify the chain development mechanism as analogous to the Nernst chain in chlorination:

$$F\cdot + H_2 \rightarrow HF + H\cdot,$$

$$H\cdot + F_2 \rightarrow HF + F\cdot + 98 \text{ kcal}.$$

Kapralova and her coworkers[38,40] have suggested that branching results from the chemical reaction of an excited molecule with a starting molecule:

$$F_2 + HF^* \rightarrow F\cdots F\cdots H\cdots F \rightarrow F\cdot + FH + F\cdot. \quad (15)$$

It may be noted that this reaction leads formally to the same result as energy transfer from an excited HF* molecule to a molecule of fluorine:

$$HF^* + F_2 \rightarrow HF + F_2^*,$$

$$F^*_2 \rightarrow 2F\cdot.$$

This type of branching mechanism by energy transfer was proposed by Semenov at a very early stage in the development of the theory of branched chain reactions[41,42], and has since been invoked by various workers[44-46]. However, it is in the chemical reaction that the most effective utilisation of large amounts of energy can be expected[37,43]. Hence, the bimolecular interaction mechanism of scheme (1) can be applied to this system, too.

According to the experimental results, reaction (15) has a much lower probability than dissipation of the energy. However, because of the very long chains in the fluorination of hydrogen, the probability is sufficient to cause non-stationary reaction and spontaneous ignition. The same mechanism can be applied to the fluorination of methane and other compounds, when the resulting molecule does not contain a sufficient amount of energy for unimolecular decomposition at the weakest bond.

Clearly, however, the more complex the resulting molecule, the less probable is bimolecular reaction with F_2, because the probability of energy concentration at the site of attack decreases[37].

4. Reactions between Organometallic Compounds and Alkyl Halides

We have considered some examples of strong oxidising agents reacting according to Semenov's scheme. We shall

now discuss the reactions of organometallic compounds, which are known to be strong reducing agents. When metal alkyls react with halogen derivatives according to scheme (1)

$$R'Hal + MR'' \rightarrow R'\cdot + MHal + \cdot R'', \qquad (16)$$

the considerable energy of the resulting ionic bond M–Hal largely balances the rupture of the relatively weak M–R'' bond and of the R'–Hal bond, so that the heat required by the elementary reaction (16) and its activation energy should both be small. Reactions between alkyl halides and organometallic compounds occur in the familiar Wurtz, Fittig, and Grignard reactions. Although the mechanism of these reactions has been studied in detail in comparatively few cases, the available information shows that the mechanism can vary according to the nature of the metal, the reactants, and the medium. Metals with a low ionisation potential (e.g. potassium) form relatively polar M–C bonds, and this gives the reaction a heterolytic character, particularly in polar solvents. On changing to metals with a high ionisation potential the polarity of the M–C bond decreases, and this, as has been shown above, favours the formation of free radicals, particularly in non-polar hydrocarbon media.

Among the alkali metals, lithium has the highest ionisation potential[47], and therefore the Li–C bond is more covalent than the Na–C and K–C bonds. Thus, free-radical formation is most likely to be found in the reactions of lithium alkyls with alkyl halides.

The free-radical mechanism of the reaction of organometallic compounds with halogen derivatives has been discussed on a number of occasions[48–53].

Bryce-Smith[54] obtained a direct proof of the formation of radicals in his work on the reactions of the metals Li, Na, K, and also butyllithium, butylsodium, butylpotassium, with butyl iodide, bromide, and chloride in the presence of cumene, which reacts with free radicals to give 2,3-dimethyl-2,3-diphenylbutane:

$$R\cdot + C_6H_5CH(CH_3)_2 \rightarrow RH + C_6H_5\dot{C}(CH_3)_2,$$
$$2\,C_6H_5\dot{C}(CH_3)_2 \rightarrow C_6H_5C(CH_3)_2C(CH_3)_2C_6H_5.$$

An appreciable amount of the dimethyldiphenylbutane is formed only in the reactions of lithium and butyllithium with butyl halides. In the reactions of sodium, potassium, butylsodium, and butylpotassium its formation was negligible. Bryce-Smith proposed the following reaction scheme:

$$C_4H_9I + 2M \rightarrow C_4H_9M + MI,$$
$$C_4H_9I + C_4H_9M \rightarrow 2\,\dot{C}_4H_9 + MI,$$
$$2\,C_4H_9 \nearrow C_8H_{18}, \quad \searrow C_4H_{10} + C_4H_8,$$
$$C_4H_9 + HS \rightarrow C_4H_{10} + \dot{S},$$
$$\left.\begin{aligned} C_4H_9M + C_4H_9I &\rightarrow C_8H_{18} + MI \\ C_4H_9M + C_4H_9I &\rightarrow C_4H_8 + C_4H_{10} + MI \end{aligned}\right\} \text{ionic path.}$$

Bryce-Smith stresses that free-radical formation is very probable when the colliding molecules take up a linear configuration R...Li...X...R, so that the alkyl groups are as remote from each other as possible. Formation of free radicals was demonstrated in a similar way by Okhlobystin and his coworkers[55], who studied the reaction of organomagnesium compounds with alkyl halides in hydrocarbon solvents. In their work on the reaction between butylmagnesium iodide and butyl iodide and chloride in cumene, they detected the formation of the dimethyldiphenylbutane, together with butane and butene, among the reaction products. They explained their results by the scheme

$$C_4H_9MgI + C_4H_9I \rightarrow 2\,\dot{C}_4H_9 + MgI_2,$$
$$2\,C_4H_9 \rightarrow C_4H_8 + C_4H_{10},$$
$$C_4H_9 + C_6H_5CH(CH_3)_2 \rightarrow C_4H_{10} + C_6H_5\dot{C}(CH_3)_2,$$
$$2\,C_6H_5\dot{C}(CH_3)_2 \rightarrow C_6H_5C(CH_3)_2C(CH_3)_2C_6H_5.$$

The mechanism of the reaction is substantially changed on passing to a polar solvent[56–58]. Thus, the reaction RMgX + R'X in ethers yields mainly RR', apparently without formation of free radicals. When the reaction is carried out in tetrahydrofuran and dimethoxyethane, alkyl exchange is observed[57]: $RMgX + R'X \rightleftharpoons R'MgX + RX$.

In general, therefore, scheme (1) by no means exhausts the mechanism of the interaction of organometallic compounds with halogen-containing molecules. Thus, the large and important class of reactions between the transition-metal halides and aluminium alkyls does not usually involve radicals as intermediates[59,60], although schemes similar to (1) have frequently been postulated[61].

The mechanism of these reactions, leading to well-known polymerisation catalysts, falls outside the scope of the present Review.

The kinetics and mechanism of the reactions between ethyllithium and a number of alkyl halides have been investigated[62–67] at the Institute of Chemical Physics of the USSR Academy of Sciences. The formation of free radicals was most unequivocally demonstrated in the reaction between ethyllithium and triphenylchloromethane[62]. The relatively low rate of recombination of triphenylmethyl radicals[68] contributed to their formation in concentrations sufficient to enable the reaction to be studied by electron spin resonance. It was found that the concentration of $(C_6H_5)_3C'$ radicals passes through a clearly defined maximum immediately after the reactants are mixed, and then drops to an equilibrium value.

The initial formation of a concentration of radicals in excess of equilibrium proves that these radicals are a primary product in the reaction:

$$(C_6H_5)_3CCl + LiC_2H_5 \rightarrow (C_6H_5)_3C\cdot + LiCl + \cdot C_2H_5. \qquad (17)$$

Kinetic investigation led D'yachkovskii and his coworkers[62] to conclude that the activation energy of reaction (17) is 4–5 kcal mole^{-1}. These workers studied the fate of the ethyl radicals, and concluded that they are formed as complexes with C_2H_5Li molecules: this makes their reactivity quite different from that of free ethyl radicals.

Similar conclusions were reached from a study[63] of the mechanism of the reaction between ethyllithium and ethyl iodide in hydrocarbon solvents. The experimental results — formation of ethane, ethylene, and butane in the reaction, formation of C_2H_5D if the reaction is carried out in deuterated solvents, and decrease in the yield of ethane in the presence of free-radical acceptors — confirm the formation of free ethyl radicals during the reaction. At the same time, a quantitative estimate of the yield of C_2H_5D and certain other facts show that only a fraction of the $C_2H_5^{\cdot}$ radicals are free: the remainder appear to be bound in a complex with ethyllithium. The explanation of this result is evidently to be found in the fact that ethyllithium is present in solution, and reacts with a molecule of alkyl halide, in the form of associated complexes[69–73]. Hence, when a C_2H_5 radical is formed from

a C_2H_5Li molecule, it is already bound to molecules of ethyllithium which form the complex.

The stability of the bond between a C_2H_5 radical and the C_2H_5Li molecules is still unknown, but it is evident that the reactivity of a radical which is bound in this way must be considerably lower than the reactivity of a free $\cdot C_2H_5$ radical formed from a C_2H_5I molecule.

Our work on the kinetics of the reactions of C_2H_5Li with ethyl iodide, bromide, and chloride, and with some other organic chlorides[66,67], has led us to conclude that the rate-determining stage is the first elementary act

$$(C_2H_5Li)_n\, C_2H_5Li + IC_2H_5 \rightarrow \cdot C_2H_5 (C_2H_5Li)_n + LiI + \cdot C_2H_5.$$

The most important kinetic results are summarised in Table 2. The most obvious conclusion from the data for different chlorides is that the reaction rate decreases and the activation energy increases as the energy of the C–Cl bond increases.

As D(R–Cl) is varied from 48 to 80 kcal mole^{-1}, the rate constant for the reaction at 90° decreases by a factor of approximately 10^5. The variation of the activation energy E with D(R–Cl) is not far from linear. Since the heat of reaction q is almost completely determined, in the reactions of different chlorides with ethyllithium, by differences in the C–Cl bond energy, the linear dependence of E_{act} on D(R–Cl) implies that E_{act} must be linearly related to q, i.e. that the Polanyi–Semenov rule is obeyed.

The numerical values of the coefficients A and α in the expression $\epsilon = A - \alpha q$ could be estimated only approximately, because of uncertainty in the value of $D(Li–C_2H_5)$ in solution. Adopting the value obtained for the gas phase[75] without allowance for molecular association, the variation of ϵ with q was described by the formula $\epsilon = 13 - 0.33q$. It is interesting to note that the values of A and α obtained in this way are not very different from the corresponding values for radical reactions.

The reactions of ethyllithium with ethyl iodide, bromide, and chloride were examined to establish the effect of the nature of the halogen on the rate of reactions of this type. In this series, the increase in the energy of the C–Hal bond is accompanied by a corresponding increase in the energy of the Li–Hal bond, so that the heats of these reactions remain approximately constant:

	D(C–Hal) (Ref. 47), kcal mole^{-1}	D(Li–Hal) (Ref. 47), kcal mole^{-1}	q, kcal mole^{-1}
C_2H_5I	51	83,6	13.4
C_2H_5Br	65	100	12.5
C_2H_5Cl	80	112,5	13.5

At the same time, the activation energy of the reaction increases considerably from C_2H_5I to C_2H_5Cl, varying linearly with the energy of the C–Hal bond. Similar changes in activation energy are observed in many series of reactions of different types, in which the energy changes associated with the rupture and with the formation of bonds are mutually compensating, so that the thermal effect does not change appreciably. Typical of these are the reactions between atomic sodium and alkyl halides[76,77], the reactions between the CF_3 radical and methyl chloride, bromide, and iodide[78], the unimolecular decomposition of alkyl halides[79,80] by the scheme $C_2H_5Hal \rightarrow C_2H_4 + HHal$, and others[81].

Thus, this type of behaviour would appear to be common to the kinetics of elementary reactions. It can be formulated in the following way: if, in a series of related reactions, the heat of reaction is approximately constant because the change in the energy of the bond undergoing fission is compensated by the corresponding change in the energy of the bond which is formed, then the activation barrier opposing the reaction increases with increase in the energy of the bonds involved in the reaction.

TABLE 2.

Reaction	log A	E, kcal × mole^{-1}	D(C–Hal) (Ref. 47), kcal mole^{-1}	20+log k_{90}
$C_2H_5Li+C_2H_5I$	6.74	13.6	51	3.561
$C_2H_5Li+C_2H_5Br$	7.08	16.3	65	2.286
$C_2H_5Li+C_2H_5Cl$	7.00*	19.0*	80	0.590
$C_2H_5Li+C_4H_9Cl$	6.97	18.8	76	0.673
$C_2H_5Li+iso\text{-}C_3H_7Cl$	7.00*	17.6*	74	1.400
$C_2H_5Li+t\text{-}C_4H_9Cl$	7.00*	13.7*	70	3.750
$C_2H_5Li+C_6H_5CH_2Cl$	4.55	10.5	61	3.225
$C_2H_5Li+C_6H_5Cl$	7.59	14.1	59	4.087
$C_2H_5Li+(C_6H_5)_3CCl$	4.32	5.0	48	5.853

* The value log A = 7.00 was assumed, and E was calculated on this assumption.

This rule has been explained[67] in terms of the increase in the steepness of the potential energy curves on passing to more stable bonds.

The existence of the relationship $\Delta E = \beta \Delta D$ points to some connection between the values of A for series of similar reactions in which the condition $\epsilon = A - \alpha q$ is obeyed, e.g. for the series of reactions between C_2H_5Li and chlorides, bromides, and iodides.

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CHAIN TRANSFER WITH FISSION

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1. INTRODUCTION

Processes leading to the formation of macromolecules can be divided into two classes — chain reactions, which include many different methods of polymerisation, and non-chain reactions, which include condensation polymerisation and stepwise reactions.

As early as 1934 Semenov defined [1] polymerisation as a non-branching chain process, and predicted the possibility of chain transfer in a polymerisation system in general, and through a polymer in particular.

More recently, as a result of advances in the chemistry of hetero-chain polymers, various highly specific — both chemically and kinetically — phenomena have been discovered.

In 1940 Flory recognised the degradation caused by the starting materials on a polymer formed by condensation polymerisation [2]. Subsequently, Korshak and his coworkers [3-5] showed that considerable interchain exchange by transesterification and transamidation occurs during the formation of polyesters and polyamides by condensation polymerisation. This phenomenon has been put to use for the synthesis of mixed polymers of the polyester, polyamide, and polyamidoester types.

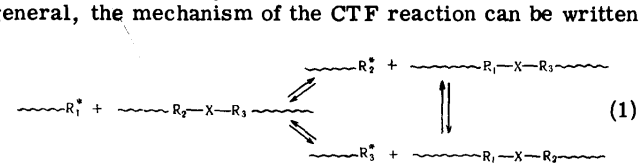
The possibility of interchain exchange was ascribed initially to condensation polymerisation processes only [3-5], and was even taken to be one of the fundamental differences between polycondensation and polymerisation processes.

However, interchain exchange is governed only by the structure of the macromolecule and by the type of active centre, and is evidently a characteristic of all hetero-chain polymers irrespective of the method of preparation. Such exchange can therefore occur in both polycondensation and polymerisation, and also with the resulting hetero-chain polymeric molecules, independently of their method of preparation.

Studies of the polymerisation and copolymerisation of trioxan [6-12] have led to the conclusion that an interchain exchange of a similar type, proceeding by a transacetalation mechanism, occurs in this system.

In 1962 Enikolopyan [8] demonstrated the possibility of interchain exchange during polymerisation by a mechanism which was subsequently called chain transfer through the polymer with fission (CTF).

Chemically, the CTF reaction consists in the exchange interaction of two molecules — one of which is an active centre and the other an inactive macromolecule — by a homolytic or heterolytic substitution mechanism. In general, the mechanism of the CTF reaction can be written



(1)

where X is a hetero-atom (O, S, N, P, Si, metal, etc.) and $\sim R_i^*$ is an active macromolecule (cation, anion, or radical).

The mechanism suggested is fairly universal, and we may assume that it applies to interchain exchange and also to the so-called "degradation" reactions between a polymer chain and the starting materials (or materials of similar nature) during condensation polymerisation. As shown by Korshak and coworkers [3,4], who made a systematic and extensive study of this reaction, interchain exchange proceeds much faster in the presence of catalysts of an acidic or basic nature. The end-groups of the starting material may have a catalytic effect on the process, but the rate of interchain exchange in this case is lower than with specially added catalysts. The exchange reaction is very strongly inhibited when it occurs between macromolecules with blocking end-groups (e.g. alkylated end-groups).

These facts strongly suggest that the reactions in question occur via some ionic states, probably as nucleophilic substitution reactions according to scheme (1).

It can be seen from the scheme that the CTF reaction should produce, during homopolymerisation, a redistribution in size of the growing macromolecules [9], and during the interaction of chemically different polymeric chains, block copolymers [10]. This reaction is one of the most general methods for modification of the main chain and side-chains of a polymer. It can be used to prepare mixed hetero-chain and carbon–hetero-chain macromolecules.

If $\sim R_i^*$ is a compound of low molecular weight the result of the CTF reaction should be a polymer with specified end-groups. This opens up wide possibilities for the synthesis of polymers and oligomers with reactive end-groups. The great practical importance of the CTF reaction in which $R_i^*\sim$ is a material of low molecular weight arises also from the possibility of synthesising thermostable polymers having a lower temperature limit of polymerisation. This method has been successfully applied to the problem of producing thermally stable polyoxymethylene.

An interesting feature of the CTF reaction is the ability of the active centre of the macromolecule to attack its own chain:

$$R_i - R_j - R_k^* \rightleftarrows R_i^* + \begin{pmatrix} R_k \\ R_j \end{pmatrix}. \qquad (2)$$

In this case a cyclic macromolecule may be formed [12]. We may also expect the formation of some very peculiar polymers having a "ring within a ring" structure (polycatenanes). If two polymers of different composition take part in a CTF reaction, copolymers will be formed without a chemical bond being involved.

The most essential feature of polymeric systems in which CTF reactions are proceeding is, as scheme (1) shows, the fact that every "dead" polymeric chain can become "alive". Also, a "dead" polymeric system can be "revived" by introducing a suitable activator. Of all the reactions known in polymer chemistry, CTF alone can bring "dead" chains into the polymerisation process without significant modification. Thus, the concept of a "live" system is more general than the definition of Szwarc [13] implies.

A detailed thermodynamic, kinetic, and chemical analysis of the CTF reaction, made in the Polymerisation Kinetics Laboratory of the Institute of Chemical Physics of the USSR Academy of Sciences, has established the uniqueness of the process, which can therefore be considered to be a new, fifth elementary act among polymerisation processes.

The present review aims to systematise and summarise existing data on the CTF reaction, and to discuss the potential applications of this reaction to polymer modification.

2. KINETIC AND THERMODYNAMIC FEATURES OF CHAIN TRANSFER WITH FISSION (CTF)

The specific feature of polymeric systems as compared with chemical substances of low molecular weight, is from the thermodynamic standpoint, their statistical nature, i.e. the existence of a definite distribution in size and composition of the macromolecules. This must undoubtedly be reflected in the nature of the processes occurring in polymer systems.

Thus, the size distribution alone will alter the entropy of the system, irrespectively of the nature of the polymeric molecules, of their state in the system, and of their interactions with each other and with the medium. Consider a reaction leading to a change in the size distribution of the macromolecules. We shall assume that the change involves only equivalent bonds: since the internal energy of the system depends on the total energy of the bonds, which is assumed to remain unchanged, and also on the interaction of the macromolecules with each other and with the medium (which depends on the total number of segments, again assumed unchanged), the reaction does not affect the internal energy of the system.

$$R_i + R_j \rightarrow R_{i+k} + R_{j-k}. \qquad (3)$$

The total entropy of the system can be split into the configurational entropy, the entropy of the segments, and the entropy of interaction of the macromolecules with each other and with the medium; the statements made above in relation to the enthalpy of the system apply also to the entropy, with the exception of the configurational entropy, whose value depends on the length of the macromolecule according to the expression

$$S_{R_j} = R \ln (a^j), \qquad (4)$$

where j is the length of the macromolecule, and a is the number of possible positions in space of a segment with one end fixed.

Since the entropy of the system is equal to the sum of the entropies of the components, the configurational entropy also must be unaffected by our reaction.

It follows from the statistical nature of a polymeric system that we must take the distributional entropy of the system into account. Strictly speaking, any physical system can be regarded as statistical from the point of view of the distribution of the various forms of energy. However, energy redistribution occurs so rapidly that, with few exceptions, the energy can be assumed to adopt an equilibrium (Boltzmann) distribution. This is not so in polymeric systems, where the distribution concerns units in macromolecules. Obviously, a redistribution of this type cannot occur unless a kinetically favourable mechanism is available. If such a mechanism is possible, the reaction will lead to the establishment of an equilibrium distribution, whose nature can be readily inferred on the hypothesis of maximum entropy. Thus, the driving force of exchange reactions of this type is an entropic one.

Taking the distributional entropy into account, we obtain for the reaction

$$\Delta S = R\left\{\ln \frac{(i+j)!}{(i+k)!\,(j-k)!} - \ln \frac{(i+j)!}{i!\,j!}\right\} = R \ln \frac{j!\,i!}{(i+k)!\,(j-k)!}. \qquad (5)$$

Solving the problem of maximum distributional entropy [14] for the conditions

$$\sum_l R_l = N; \quad \sum_l l R_l = M,$$

we find, as for the Boltzmann distribution,

$$R_l = \frac{N^2}{M}\left(1 - \frac{N}{M}\right)^{l-1} \simeq \frac{N^2}{M} e^{-\frac{N(l-1)}{M}}. \qquad (6)$$

The composition distribution of the macromolecules presents a more complicated problem, because the structure of the copolymer must affect both the internal energy of a macromolecule and its entropy. Thus, even in the presence of a mechanism leading to redistribution, maximum distributional entropy may not be achieved owing to the increase in internal energy or to the decrease in entropy of the macromolecules themselves.

Clearly, redistribution of the sequences A...A and B...B within a chain involves breaking A–A and B–B bonds and the creation of two A–B bonds, or *vice versa*. For each exchange of this kind the expenditure (or gain) of energy is given by

$$\Delta E = 2\left(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2}\right), \qquad (7)$$

so that the redistribution will be influenced not only by the distributional entropy but also by the change in internal energy. In the limiting case when

$$\epsilon_{AB} \ll \frac{\epsilon_{AA} + \epsilon_{BB}}{2}, \qquad (8)$$

there will obviously be no redistribution at all, in spite of the evident loss of distributional entropy.

Chain transfer with fission is the kinetic mechanism which allows attainment of the most probable distribution, corresponding to maximum entropy. Alternative mechanisms are possible, of course, but the reactions encountered in polymer chemistry either involve fundamental changes in the system [15-17] or operate only on macroradicals or macroions, i.e. on the "live" part of the macromolecule, without affecting the "dead" parts (reversible polymerisation).[18]

The special kinetic status of CTF was first pointed out by Enikolopyan and his coworkers [8,9]. From a study of interchain exchange in a system consisting of R molecules of mean degree of polymerisation $\bar{P}$ with all end-groups active, i.e. of the reaction

$$R_i + R_j \rightarrow R_{i+e} + R_{j-e}, \qquad (9)$$

they arrived [9] at the kinetic equation for the concentration of the $j$mer

$$\frac{dR_j}{dt} = -2kR_jR - 2kR_j\sum_1^N iR_i + 2k\sum_{i=j}^N\sum_{e=j}^N R_iR_e + 2k\sum_1^j\sum_{j-i}^j R_iR_e + 4k\sum_{i=j}^N\sum_1^N R_iR_e, \qquad (10)$$

the coefficient k being independent of j, i, and e.

At equilibrium

$$\frac{dR_j}{dt} = 0. \qquad (11)$$

The equation gives for R_j

$$R_j = \frac{R}{\bar{P}}\, e^{-j/\bar{P}}. \qquad (12)$$

This implies that, independently of the initial distribution, CTF leads to a Semenov–Flory distribution [1,21]

as calculated for equilibrium polymerisation and polycondensation. It can be shown that under these conditions

$$\frac{\bar{P}_w}{\bar{P}_N} = 2.$$

The attainment of this distribution was experimentally demonstrated by studying the cationic exchange between low-molecular-weight dimethyl ethers of poly(oxymethylene glycol)[19], because the molecular-weight distribution is difficult to determine for high-polymer samples.

Disproportionation of the dimethyl ether of dioxymethylene glycol (degree of polymerisation $P = 2$) on treatment with 0.06% sulphuric acid at 120° causes the appearance of a whole series of oligomers, beginning with dimethoxymethane, in amounts independent of both catalyst concentration and temperature. The fact that the resulting composition is independent of the experimental conditions suggests that the observed distribution is an equilibrium one.

The distribution obtained cannot be compared with the function (5), because the latter was derived for the case of $j \gg 1$; in the case of oligomers we cannot ignore the length of one of the two monomeric units in comparison with the length the entire molecule.

The distribution function for oligomers of low molecular weight was obtained by a statistical method, which led to expression (6), obtained previously by a thermodynamic method (p. 309):

$$R_n = \left(\frac{1}{2}\right)^n = e^{-0.69n}. \qquad (13)$$

This equation satisfactorily describes the experimental results.

Thus, it has been shown both theoretically and experimentally that CTF leads to the most probable molecular-weight distribution.

It should be noted that these results have been obtained on the assumption that the rate constant of CTF is independent of the degree of polymerisation of the attacking active molecule and of the molecule being attacked, i.e. that it does not depend on the site of attack. This assumption can be unambiguously substantiated only on the basis of kinetic data. To this end, the kinetics of the establishment of equilibrium was investigated[20] for the disproportionation of the dimethyl ether of dioxymethylene glycol, using the boron trifluoride–ether complex as catalyst.

Evaluation of the kinetics based on a scheme analogous to (3)

$$R_e^* + R'_m - O - R'_n \rightarrow R_m^* + R'_e - O - R'_n,$$

where R'_i is a free-radical residue of structure $CH_3-[OCH_2]_i-$ and R_i^* is a carbonium ion of corresponding structure or a radical forming part of an oxonium ion

$$R'_i - \overset{+}{O}\begin{matrix} R'_m \\ \diagdown \\ R'_n \end{matrix}.$$

The set of kinetic equations corresponding to the proposed scheme is

$$\frac{dR_n}{d\tau} = R\sum_{i=1}^{n} R_i^* - \sum_{e=1}^{n-1}\sum_{i=1}^{n-e} R_i R_e^* - nR_nR^*, \qquad (14)$$

$$\frac{dR_n^*}{d\tau} = \left(R - \sum_{i=1}^{n-1} R_i\right) R^* - \bar{n}RR_n^*,$$

$$d\tau = 2kdt$$

where R_i is the concentration of $CH_3-[OCH_2]_i-OCH_3$ molecules,

R is the total concentration of all molecules,

R_j^* is the concentration of active centres,

n is the mean number of $-OCH_2-$ groups per molecule,

and k is the rate constant for interaction between an active centre and a neutral molecule (assumed independent of R_e^*, R'_m, and R'_n).

This system can be solved step by step. The following expressions are obtained for the first three terms (n = = 1, 2, 3)

$$R_1 = R\left(\frac{1}{2} - \frac{1}{2}e^{-R^*\tau}\right),$$

$$R_2 = R\left(\frac{1}{4} + \frac{1}{2}e^{-R^*\tau} + \frac{1}{4}e^{-2R_\tau^*}\right),$$

$$R_3 = R\left(\frac{1}{8} + \frac{1}{8}e^{-R^*\tau} - \frac{1}{8}e^{-2R^*\tau} - \frac{1}{8}e^{-3R^*\tau}\right). \qquad (15)$$

The following formula gives the total concentration of the remaining molecules

$$R_{rem} = R\left(\frac{1}{8} - \frac{1}{8}e^{-R^*\tau} - \frac{1}{8}e^{-2R^*\tau} + \frac{1}{8}e^{-3R^*\tau}\right). \qquad (16)$$

These equations fully represent the experimental results, the best agreement being obtained with a rate constant of $k = 0.021$ litre mole^{-1} s^{-1}. The agreement between theory and experiment confirms the authors' original assumption of the equivalence of all the acetal bonds.

The role of CTF in the various stages of the process is one of the most important problems in polymerisation kinetics. It is obvious that, in the absence of a chain-growth reaction, CTF must lead to a Semenov–Flory distribution[1,21], but chain growth will perturb this distribution in such a way that at very low rates of CTF (in the absence of chain termination and chain transfer, and with instantaneous initiation) the molecular-weight distribution will be described by Poisson's law[18]

$$R_j = \frac{\bar{P}^j}{j!}e^{-\bar{P}}. \qquad (17)$$

We shall estimate the relative velocities of these reactions.

The rate of the growth reaction is

$$w_{gr} = k_{gr}RM_0(1-\alpha), \qquad (18)$$

where α is the extent of reaction, R the concentration of active centres, and M_0 is the initial concentration of monomer.

The rate of the CTF reaction is

$$w_{CTF} = k_{tr}RM_0\alpha. \qquad (19)$$

The closeness with which the molecular-weight distribution in the system approaches an exponential distribution will be determined by the ratio of the velocities:

$$\frac{w_{CTF}}{w_{gr}} = \frac{k_{tr}}{k_{gr}}\frac{\alpha}{1-\alpha}. \qquad (20)$$

We must remember, however, that the chain growth reaction alters the length by one unit, whereas the CTF reaction alters it by an amount of the same order as the chain length, so that the velocity ratio should be multiplied by the mean degree of polymerisation $\bar{P}$. Thus the transfer intensity factor is

$$\varphi = \varepsilon\bar{P}\frac{\alpha}{1-\alpha}.$$

It is evident that the relative intensity of CTF increases sharply towards the end of the polymerisation process. A study of the polymerisation of tetrahydrofuran has, indeed, shown that the role of CTF, detected by the increase in viscosity of the system, is particularly

noticeable at the very end of the polymerisation, when the growth reaction has practically ceased[22].

Berlin and his coworkers [12] have considered theoretically the possibility of cyclisation by scheme (2) during CTF. They have derived an equation for the molecular-weight distribution in the system with allowance for the formation of cyclic structures

$$h_j = \frac{\alpha}{\beta} \cdot \frac{1}{j^{5/2}} e^{-j/l}, \qquad (21)$$

$$N_j = \frac{N}{l} e^{-j/l},$$

where l is the mean degree of polymerisation of linear molecules, h_j and N_j are the concentrations of cyclic and of linear molecules of length j, and α and β are the rate constants for cyclisation and interchain exchange respectively.

Analysis of the equations yields a number of interesting conclusions. Fig. 1 shows the variation of the mass of cyclic macromolecules for different values of the parameter

$$\varepsilon = \frac{mN}{h_0}, \qquad (22)$$

where

$$h_0 = \lim_{l\to\infty} \int_m^\infty e^{-j/l} \frac{dj}{j^{5/2}} = \frac{\alpha}{\beta} \frac{2}{\sqrt{m}},$$

is the limiting amount of monomer in the cyclic molecules.

From Fig. 1 it is evident that for $M_0 < h_0$ practically the whole of the polymer is cyclic and for $M_0 > h_0$ the mass of cyclic polymer is practically constant. Estimated values of h_0 and ϵ are 4×10^{21} cm^{-3} and 10^{-3} respectively. Thus, in some cases the polymer can be almost completely converted into a cyclic state.

Consideration of the overall molecular-weight distribution gives for $\overline{P}_w/\overline{P}_N$ the expression

$$\frac{\overline{P}_w}{\overline{P}_N} = \frac{2}{3}\left(1 - \frac{h_0}{M_0}\right)^2 \frac{1}{\varepsilon}, \qquad (23)$$

which shows that cyclisation may be a possible cause of the great polydisperseness of polymerisation products.

Recent experimental studies of the polymerisation of heterocyclic compounds[23-27], and earlier work on condensation polymerisation[28-31], have shown that large rings can be formed under these conditions.

The possibility of CTF in a system leads to redistribution of the macromolecules with respect to composition as well as to length. Plechova et al.[10] discuss the influence of CTF on the composition of copolymers.

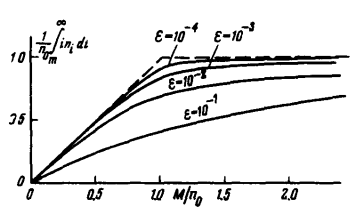


Fig. 1. Variation of mass of cyclic macromolecules with polymer concentration for different values of the parameter ϵ. [12]

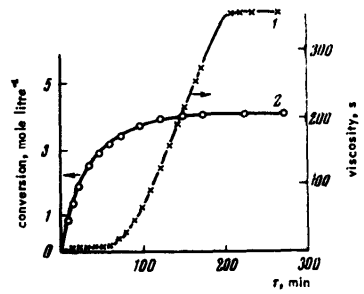


Fig. 2. Dependence of the viscosity of the polymerisation medium (1), and of the extent of reaction (2), on the duration of polymerisation of tetrahydrofuran in diethyl ether at 20° in the presence of the catalytic system

$(C_2H_5)_2O.BF_3$ —— $CH_2-CH-CH_2Cl$ (O)

with $[M]_0 = 7.0$ M, $[cat]_0 = 0.02$ M (after Rozenberg[22]).

The CTF reactions occurring in the case of a binary copolymer can be summarised as follows:

$$\sim\sim A^* + \sim\sim A-B \sim\sim \xrightarrow{k_1} \sim\sim A-A \sim\sim + \sim\sim B^*$$
$$\sim\sim A^* + \sim\sim B-B \sim\sim \xrightarrow{k_2} \sim\sim A-B \sim\sim + \sim\sim B^* \qquad (24)$$
$$\sim\sim B^* + \sim\sim A-B \sim\sim \xrightarrow{k_3} \sim\sim B-B \sim\sim + \sim\sim A^*$$
$$\sim\sim B^* + \sim\sim A-A \sim\sim \xrightarrow{k_4} \sim\sim A-B \sim\sim + \sim\sim A^*$$

It is clear that the composition of the copolymer undergoes a change: sequences (blocks) of units of a given kind can be split, and conversely separate blocks of a given unit can become "fused" into a single block. Thus, CTF can cause redistribution of the units of a copolymer among blocks and affect the number of blocks in the macromolecule.

By analogy with the number average degree of polymerisation, we can introduce the parameters S_A and S_B, the mean lengths of the blocks ~A...A~ and ~B...B~. If the average number of blocks of a given type in the macromolecule is l, it readily follows that

$$S_A = \frac{m_A}{l}, \quad S_B = \frac{m_B}{l},$$

where m_A and m_B are the respective numbers of A and B units in the molecule.

Solving the set of differential equations for the variation in l and $[A^*]$, we obtain for equilibrium the following equation

$$l^2 - \kappa[m_A - l][m_B - l] = 0, \qquad (25)$$

where

$$\kappa = \frac{k_2 k_4}{4 k_1 k_3}.$$

When $\kappa = 1$ the expression for l takes the form

$$l = \frac{m_A m_B}{m_A + m_B} \qquad (26)$$

and

$$\overline{S}_A = 1 + \frac{m_A}{m_B}, \quad \overline{S}_B = 1 + \frac{m_B}{m_A}. \qquad (27)$$

This means that monomer units in the copolymer which are present in small numbers as compared with the other component are distributed singly.

Eqn. (26) can be obtained by a purely statistical approach[32,33].

Thus the occurrence of CFT in a system must cause a redistribution of the monomer units in the system irrespective of the initial distribution.

In the absence of CTF the average length of the blocks is completely determined by the copolymerisation constants according to the formulae

$$\bar{S}_A = r_1\varepsilon + 1; \quad \bar{S}_B = \frac{\varepsilon}{r_2} + 1. \qquad (27')$$

Discrepancies between the experimental composition of a copolymer and that calculated from the formulae (27') have been reported in papers on the copolymerisation of dioxolan with styrene[34] and of 3,3-bischloromethyl--oxacyclobutane with β-propiolactone[35]: obviously, this can be ascribed to the occurrence of CTF in these systems.

Analysis of copolymerisation kinetics with allowance for CTF leads to expressions for the rate and for the composition of the copolymer which differ from the classical expressions.

For small extents of reaction, when the consumption of monomer can be ignored, and $k_2 = 0$, we obtain

$$\alpha + \frac{k_{12}\varepsilon}{k}\left(1 - \frac{k_{21}}{K_{11}}\right)\ln\left\{1 + \frac{k_1 x}{k_{21} + k_{12} n \dfrac{k_{21}}{k_{11}}}\right\} = K_{11}C_0 t, \qquad (28)$$

where

$$\alpha = \frac{m_A}{A}; \quad n = \frac{B}{A}.$$

In the absence of CTF, the parameter α varies linearly with time:

$$\alpha = k_{11}Ct_0\,\frac{1 + k_{12}/k_{11}\cdot n}{1 + k_{12}/k_{21}\cdot n}, \qquad (29')$$

whereas if transfer through the polymer is substantial

$$\alpha = k_{11}kC_0 t. \qquad (29'')$$

The physical significance of these relationships is clear: CTF leads to a greater number of active centres of type A* than in the case of ordinary copolymerisation; this increases or decreases the rate of accumulation of the component A according as $k_{11} \gtrless k_{21}$, since

$$\frac{1 + k_{12}/k_{11}\,n}{1 + k_{12}/k_{21}\,n} \gtrless 1.$$

It is evident that the change in the rate of polymerisation of each of the components in the presence of CTF (as compared with the classical scheme of copolymerisation) will cause departures from the Mayo–Lewis composition equation[36,37].

Thus the instantaneous composition of the copolymer in the presence of CTF is given by the equation[36]

$$n = \frac{1}{2}\left[\frac{\varepsilon r_1 r_3 - r_2 r_4}{r_3} - \frac{\varepsilon + r_2}{r_3}\left(\frac{1}{\alpha} - 1\right) + \sqrt{\left[\frac{\varepsilon r_1 r_3 - r_2 r_4}{r_3} - \frac{\varepsilon + r_2}{r_3}\left(\frac{1}{\alpha} - 1\right)\right] + 4\left[\frac{r_4}{r_3} + \frac{r_1\varepsilon}{r_3}\left(\frac{1}{\alpha} - 1\right)\right]}\right], \qquad (30)$$

where r_1 and r_2 are the copolymerisation constants, and

$$r_3 = \frac{k_1}{k_{21}}; \quad r_4 = \frac{k_2}{k_{12}}; \quad n = \frac{m_A}{m_B}; \quad \varepsilon = \frac{A_0}{B_0}, \alpha = \frac{m_B}{B_0}.$$

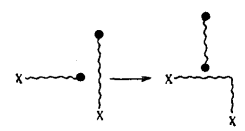
In the absence of CTF ($r_3 = r_4 = 0$) Eqn. (30) becomes identical with the classical equation for the instantaneous composition of a copolymer. If either of the parameters r_3 and r_4 is non-vanishing, the composition given by formula (30) can deviate very significantly from the classical composition. The difference increases with increase in α.

A remarkable consequence of the occurrence of CTF in a system is the special form of the "live" state of the system. The "live" state of polymers, discovered and investigated by Szwarc[13], depends on the absence of any reactions which destroy active centres or cause chain limitation in general, and thus can occur only in absolutely pure systems. This state is characterised by a molecular-weight distribution of the Poisson type[18], a linear increase in degree of polymerisation with extent of reaction, and rigid adherence to the expression

$$\bar{P}_N = \frac{\Delta M}{C}, \qquad (31)$$

where C is the total quantity of active centres, ΔM the amount of polymerised material, and $\bar{P}_N$ the mean degree of polymerisation.

As was stated above, CTF leads to an exponential molecular-weight distribution irrespective of the detailed mechanism of polymerisation. The broken macromolecules take part in CTF without disturbing the distribution, as is the case with normal "live" polymers. Molecules having "dead" end-groups on both sides can acquire active terminations as a result of CTF. As can readily be shown, this should produce chains both ends of which are active:



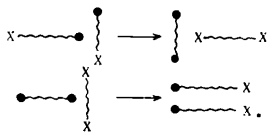
(32)

Therefore, all molecules, both "live" and "dead", will take part in reactions of chain growth, since there will be a constant exchange of end-groups between the macromolecules. Thus, in a way, all molecules in the system are "live", whatever the nature of their end-groups.

Studies of the variation in molecular weight with extent of reaction in the polymerisation of trioxan[38,39] have shown that the viscosity molecular weight increases linearly with extent of conversion, suggesting that the polyoxymethylene molecules are live[38]. However, later experiments revealed a temperature dependence of the slope of the linear plot of $\bar{M}_w$ against extent of reaction, which was unrelated to differences in the degree of initiation[38]. This provides unambiguous proof of the presence of chain--limiting reactions in the system, probably by transfer to impurities with a rate constant much higher than the growth rate constant. The linear variation of the viscosity--average molecular weight with extent of reaction can be retained only in the presence of intense CTF, which allows all the molecules to take part in chain growth and maintains proportionality between number-average and weight--average molecular weights. Thus, this special form of the "live" state of the molecules manifests itself in the polymerisation of trioxan.

It is interesting to consider the nature of the distribution of end-groups among the chains. If the macromolecules can have only two types of end-groups (active and inactive), the system will be composed of three types of molecule: — both end-groups active (A), only one active (B),

and both inactive (C) — transition of molecules of one type into another type occurring by the scheme



(32′)

The set of equations describing this process is

$$\frac{dA}{dt} = \frac{dC}{dt} = -2\frac{dB}{dt} = \frac{1}{2}kB\sum jB_j - 2kA\sum_j jC_j,$$
$$2A + B = a;$$
$$2C + B = b, \qquad (33)$$

where a is the total concentration of active groups, and b of inactive groups.

Assuming that CTF results in the establishment of an equilibrium molecular-weight distribution, and also an equilibrium distribution of end-groups, the former being observed not only in the system as a whole but also in each group of molecules, we obtain

$$\frac{A}{A+B+C} = \frac{a^2}{(a+b)^2};\quad \frac{B}{A+B+C} = \frac{2ab}{(a+b)^2};\quad \frac{C}{A+B+C} = \frac{b^2}{(a+b)^2}. \qquad (34)$$

It should be noted that this distribution of end-groups can be obtained from purely statistical considerations, by assuming that the probability of finding any group at one end of a chain is equal to its fraction of the total number of ends, whilst the probability of finding any two groups at the two ends of a chain is equal to the product of the separate probabilities for each of the groups. The fraction of macromolecules of a given type is determined by the probability of their formation.

A kinetic analysis of the exchange between molecules having more than two types of end-group is fairly complicated, but it leads to a similar result.

As the above considerations show, the kinetic and the probability approaches to the distribution of macromolecules with respect to length, composition, and type of end-groups give identical results, because of the entropic nature of CTF.

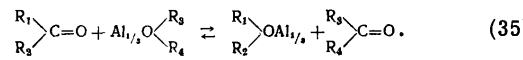
3. CTF AS AN EXCHANGE REACTION

It is possible to set up a simple and convenient model of CTF reactions on the basis of low-molecular-weight compounds simulating the functional groups which can undergo CTF (fragments of the main chain or of a side-chain of the polymer). These model exchange reactions must satisfy a number of requirements arising from the specific chemical features of CTF reactions in macromolecular compounds.

The reactions must be reversible. This is because a necessary condition for this reaction to occur during polymerisation is that the new active centre formed after the act of transfer must be able to carry on the polymerisation and CTF process. When CTF occurs, the rate constants for M_1^* with respect to M_1–M_1 and M_2–M_2, and also for M_2^* with respect to M_1–M_1 and M_2–M_2, will be different for the different homopolymers, but it is necessary that all these reactions should take place — which means, in practice, that the reaction must be reversible — in order that CTF can occur.

A second important requirement of the model reactions of exchange interaction is adherence to the principle of conservation of functional groups. This means that the functional groups initially present must not undergo any chemical change during the reaction: only radicals bound to the functional groups are exchanged.

In view of the latter requirement, we must exclude those exchange reactions which, though formally resembling model exchange reactions, follow a quite different mechanism, involving changes in the functional groups during the process. For example, reactions which do not satisfy the above conditions, although formally very similar to model reactions for CTF, are the Meerwein–Ponndorf–Verley reaction of ketones and the Oppenauer oxidation of alcohols[40]

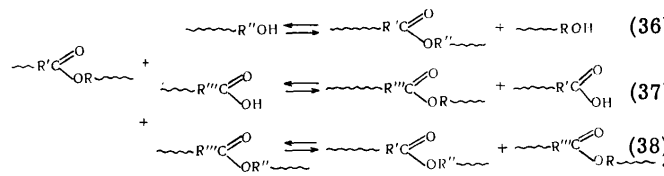


(35)

Another example of a reaction of this type is transamination, discovered by the Soviet biochemists Braunshtein and Kritsman[41].

At the present time, hardly any papers have been published on the detailed mechanism of exchange reactions, but some general features observed in studies of transesterification processes and in particular the alcoholysis of carboxylic esters[42–58] justify the statement that these are fairly typical of nucleophilic substitution processes at a carboxy-group[59,60].

We shall consider some model reactions of exchange interaction. The examples below are given merely as an illustration, and are by no means comprehensive. One of the most thoroughly investigated model reactions is transesterification. It can be conducted in three ways — (1) by reaction between an ester and an alcohol (alcoholysis), (2) by reaction between an ester and an acid (acidolysis), and (3) by reaction between two esters (esterolysis):



(36)

(37)

(38)

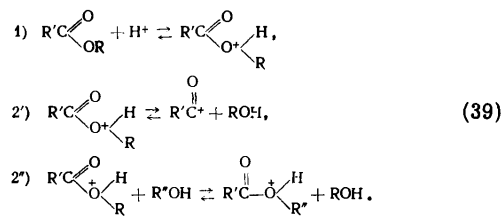
Reactions (36) and (37) simulate the reaction between a polyester macromolecule and a low-molecular-weight impurity (acid or alcohol); reaction (38) simulates the interchain exchange of two polyester macromolecules.

The rate of reactions (36) and (37) is considerably increased by acidic or basic additives[44,46,61], while reaction (38) is accelerated by acidic catalysts[45,61]. Studies of alcoholysis have shown[49] that a heavier hydrocarbon radical displaces a lighter one, but on occasions a heavier alcohol radical is displaced by a lighter one in fairly high yield, as in the alcoholysis of bornyl acetate by ethanol and by butanol[47]. The structure of the radical R′ has a major effect on the rate of exchange. Thus, the exchange is strongly retarded by the presence of double bonds in the α and β positions with respect to the carboxy-group, as in crotonic and cinnamic esters[44]. Conversely, electron-acceptor groups in the α position to the carboxyl increase the rate of exchange[44].

It has recently been shown[56] that the yield of alcoholysis products is practically unaffected by the number and complexity of the substituents in the acid part of malonic esters.

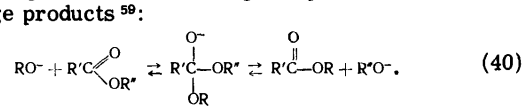
The relative reactivity of various radicals in the alcoholysis of acetates has been measured[50]. As was to be expected, primary alcohols are the most reactive, followed by secondary alcohols.

Korshak and Vinogradova[61] studied the kinetics of alcoholysis in the exchange between ethyl stearate and cetyl alcohol. The reaction takes place even in the absence of catalysts, but very high temperatures are then necessary. Alkaline (sodium hexadecyloxide) and particularly acid (concentrated sulphuric acid) catalysts allow the temperature to be lowered appreciably whilst increasing the velocity above that of the uncatalysed reaction. The mechanism of the uncatalysed (or acid-catalysed) alcoholysis, like that of the thoroughly investigated hydrolysis of esters under analogous conditions[62], appears to consist in the rapid formation of an acylalkyloxonium ion, which subsequently decomposes to form an acylium cation or reacts with the alcohol:



(39)

The mechanism of alkaline alcoholysis involves initial attack by an alkoxy-anions on the carboxyl carbon atom, which has a partial positive charge as a result of the electron-acceptor effect of the carbonyl group. The resulting anionic intermediate can decompose in two ways — to regenerate the starting compounds or to form the exchange products[59]:



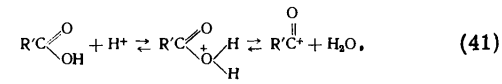
(40)

Some unusual features were observed in a study of the alcoholysis between ethyl stearate and acetic acid[63]. It was shown that the order of the reaction changes from first to second during the course of the reaction.

Acidolysis is accelerated by protonic and aprotic acids[64]. It is very important in synthetic chemistry, and is widely used for the preparation of vinyl esters of carboxylic acids from vinyl acetate[65].

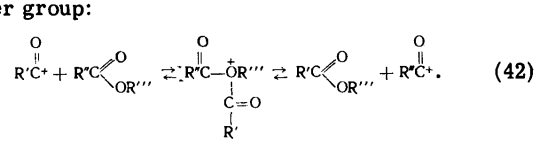
As in the previous systems, the uncatalysed exchange between two esters occurs very slowly and only at sufficiently high temperatures[66]. The reaction becomes much faster in the presence of alkaline, and even more so in the presence of acidic, catalysts[66-68]. The rate of the reaction is proportional to the concentration of the reagents[66].

The mechanism of acid-catalysed acidolysis evidently involves initial formation of an acylium cation



(41)

which can then attack a molecule of the ester with exchange of the ester group:

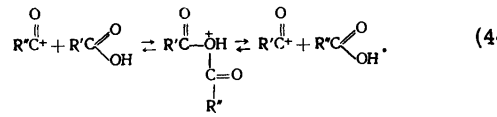


(42)

Regeneration of $O{=}C^{+}R'$ can occur either through the interaction of $O{=}C^{+}R''$ with water

(43)

followed by reaction (41), or directly by reaction between $O{=}C^{+}R''$ and the acid



(44)

In addition to the Soviet work discussed above[61,63,66], we must mention that papers of Flory[2,69], who showed that the alcoholysis of poly(decamethyleneadipate) under the influence of small amounts of an alcohol or a glycol (decamethylene glycol or dodecan-1-ol) follows first-order kinetics in the presence of an acid catalyst. The reaction velocity is proportional to the concentration of the acid catalyst. The activation energy of the alcoholysis is 11.5 kcal mole^{-1}. It was also shown that the exchange reaction in question is approximately 11 times as slow as the polyesterification of decamethylene glycol and adipic acid.

Various workers[70-72] have found that these exchange reactions follow second-order kinetics, the activation energy of the uncatalysed exchange being 20–30 kcal × × mole^{-1} higher than that of the acid- or base-catalysed reaction by factors of 2–3.

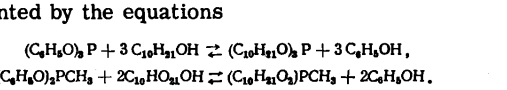
On the basis of the kinetic results obtained in their study of transesterification on model compounds, Korshak and Vinogradova[73,74] arranged the reactions in order of increasing relative reaction rate as follows: esterolysis < < alcoholysis < acidolysis. We should note, however, that in the condensation polymerisation process used in the synthesis of polyesters the relative importance of acidolysis and alcoholysis decreases as the reaction proceeds, owing to the loss of functional groups, while esterolysis becomes increasingly important as a result of the accumulation of polymeric products.

Transesterification occurs readily also with the esters of phosphoric, phosphorous, and phosphonic acids[75-80]. The preparation of dialkyl phosphites from diphenyl phosphites by an exchange reaction between the latter and aliphatic alcohols was worked out by Petrov et al.[75] The reaction proceeds by the scheme

(45)

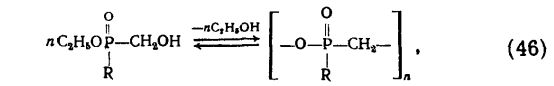
The reaction product is formed in fairly high yield, reaching 93%.

Good yields of exchange products have been obtained also in the transesterification of aromatic esters of phosphoric and phosphonic acids with aliphatic alcohols[76]. The reaction is catalysed by alkali-metal alkoxides and is represented by the equations



Nifant'ev and Fursenko[77] found that the transesterification of phosphites and phosphonites, a very important synthetic reaction used in the preparation of many phosphorus derivatives, can be carried out under much milder conditions (20–40°) and without a catalyst if the 2-fluoroethyl esters of tervalent phosphorus acids are used as starting compounds.

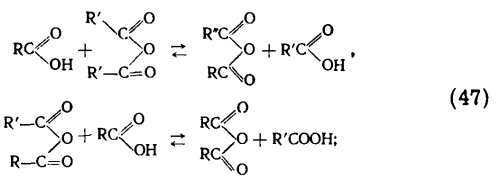
Pudovik and Evstaf'ev [78,79] used transesterification to prepare polyphosphites and polyphosphinites by the reaction of phosphinic and phosphinous esters with glycols. In a recent paper [80], these authors have extended this method to the preparation of phosphorus-containing polymers by homopolyesterification:



(46)

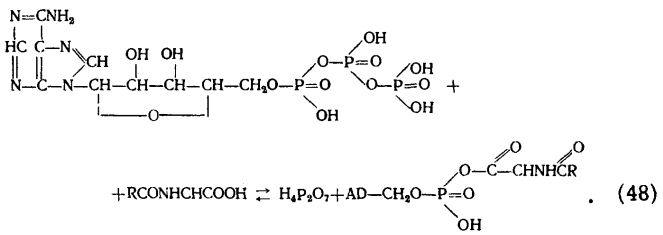
where R = OC_2H_5, C_2H_5, C_6H_5. The kinetics of this reaction is described by a second-order equation, with an activation energy of 23 kcal $mole^{-1}$.

A very important reaction in synthetic chemistry is the exchange interaction of carboxylic acids with acid anhydrides [81-85], leading to formation of the anhydrides of the corresponding acids or to mixed anhydrides:



(47)

The formation of a mixed anhydride is thought [86] to be one of the essential intermediate stages in the synthesis of polypeptides and proteins. Adenosinetriphosphoric acid, which can be said to contain an inorganic acid anhydride group, exchanges with an acylamino-acid to form a mixed anhydride — the acyladenylate of the amino-acid, which can then be used *in vivo* or *in vitro* to construct a peptide link:



(48)

The transetherification of an ether or acetal linkage also has great practical importance in the synthesis of various ethers and acetals [87-94]. These reactions, which proceed according to the scheme

$$ROR + R'OR' \rightleftarrows 2ROR',$$

are catalysed as a rule by acid substances — protonic [94] and aprotic [89] acid, ion-exchange resins [91], and other compounds [89,90] — being particularly important in the synthesis of natural products, especially polysaccharides, in which interchain exchange occurs through the splitting of a glucoside link under the influence of specific enzymes [86].

Exchange reactions between the amide group and acids, amides, esters, and amines are quite rapid. These reactions are of the utmost importance in biosynthesis, and will be dealt with separately.

The disulphide group, and polysulphide groups in general [95], are very reactive towards a number of exchange interactions. The most typical exchanges of this type are the thiol–disulphide and disulphide–disulphide, which can be represented by the general equations

$$RSSR + R'SH \rightleftarrows RSSR' + RSH; \quad (49)$$

$$RSSR + R'SSR' \rightleftarrows 2R'SSR. \quad (50)$$

It is interesting to note that these reactions can be initiated both by anionic and by cationic catalysts. In a few cases the exchange can occur also by a radical mechanism. Thus, for example, exchange was reported [96] between dodecanethiol and propyl disulphide merely on heating, without the addition of any activators.

The thiol–disulphide exchange is very strongly accelerated in the presence of alkaline catalysts [97]. The polarity of the solvent has a considerable effect on the rate of exchange. It has been shown [98] that an exchange which is slow in absolute methanol is accelerated by aqueous methanol, and goes very rapidly in the presence of alkali. The rate of the thiol–disulphide exchange in methanol at 0–35° is proportional to the concentration of disulphide and the alkyl sulphide ion, and the activation energy [99] is 15 kcal × × $mole^{-1}$. Reactants containing sterically hindered groups, such as 2-methylpropane-2-thiol reacting with di-t-butyl disulphide, exchange very slowly, with an activation energy of ~ 22 kcal $mole^{-1}$.

Entirely different behaviour is observed when the thiol–disulphide exchange is carried out in non-polar media. The exchange interaction between aliphatic thiols and disulphides in an aromatic hydrocarbon medium is very slow even at 200°. Its activation energy is 28 kcal $mole^{-1}$. Yet the exchange of aromatic thiols and disulphides under similar conditions is quite fast even at much lower temperatures, and has an activation energy of ~ 10 kcal $mole^{-1}$. The reaction rate is proportional to the square root of the concentration of disulphide, and is independent of the thiol concentration. Gur'yanova and her coworkers [100] proposed a radical exchange mechanism in non-polar media to explain these facts

$$\begin{aligned} RSSR &\rightleftarrows 2RS^{\cdot}, \\ RS^{\cdot} + R'SH &\rightleftarrows R'S^{\cdot} + RSH, \\ R'S^{\cdot} + RS^{\cdot} &\rightleftarrows R'SSR; \end{aligned} \quad (51)$$

The presence of radicals was demonstrated by the accelerating effect of ultraviolet radiation and by reaction with 2,2-diphenyl-1-picrylhydrazyl. The exchange is catalysed by peroxides and azoisobutyronitrile [95]. The decomposition of acyl peroxides occurs in a similar way [34]. A radical mechanism has been postulated also for the exchange of disulphides [101]: unsymmetrical aromatic disulphides undergo rearrangement to symmetrical disulphides in boiling dioxan solutions, under ultravoilet irradiation, or on heating to 170°.

Disulphides exchange very readily in polar media in the presence of hydrogen sulphide or alkyl sulphide anions [97,102,103]. Disulphide exchange can occur also in the presence of protonic or aprotic acids [97,104,105]. The sulphonium ion is assumed to be active species.

Space does not allow us to discuss all the many exchange interactions which can be applied to polymeric molecules for the purpose of modifying them. We shall point out only that the use of nuclear magnetic resonance methods in recent years has helped to demonstrate the occurrence of exchange reactions in the most varied systems [106-109].

4. METHODS OF DETECTING CTF

Exchange reactions involving macromolecular compounds occur by essentially similar processes. Just as with other chemical transformations of macromolecular

compounds [110], the morphology of the polymer plays an important part. This is obviously a highly significant factor in reactions of this type, and exerts a strong influence on the reactivity of polymers.

The occurrence of CTF in a system can be detected in a number of ways. For a CTF reaction to manifest itself in the synthesis of a polymer by condensation or addition polymerisation, the rate constant of the CTF step must be comparable with the rate constant of the polymer formation reaction. This criterion becomes less essential when we are dealing with CTF between two existing homopolymers, since in this case the exchange can be considerably intensified by raising the temperature.

A strict chemical proof of the presence of CTF may be provided by the very fact that block and graft copolymers are formed under conditions offering no conceivable mechanism for their formation other than CTF.

Two methods of synthesis of block copolymers based on CTF have been developed. In the first method the block copolymer is synthesised by the polymerisation of one monomer in a medium of the other homopolymer [111,112], when polymerisation is accompanied by CTF. Block copolymers synthesised by this method and the methods used to identify them are listed in Table 1.

In the second method, block copolymers are synthesised by initiating CTF between the two homopolymers. It is evident that in this case we have no polymerisation as such, and that only CTF processes take place according to the scheme

$$\sim\!\sim R_jOR_i\sim\!\sim + \sim\!\sim R_kOR_l\sim\!\sim \longrightarrow \sim\!\sim R_jOR_k\sim\!\sim + R_lOR_i\sim \quad (52)$$

The results of these syntheses [113] are set out in Table 2.

Pairs of homopolymers were chosen such that one of the polymers was insoluble in the solvent used, thus enabling the occurrence of CTF to be detected visually by the gradual swelling followed by dissolution of the insoluble polymer. Blank experiments without the catalyst (to check whether the insoluble homopolymer was soluble in a solution of the other homopolymer) and without the soluble homopolymer (to check whether the polymer was soluble when degraded by the catalyst) gave no such effect. In both cases, the insoluble polymer was regenerated in almost quantitative yield.

TABLE 1. Preparation of copolymers by cationic polymerisation of a monomer in the presence of other polymers [11].

Monomer	Polymer	Type of polymer formed	Method of identification
Trioxan	polydioxolan	block copolymer	kinetic
Formaldehyde	»	ditto	»
Trioxan	poly(ethylene oxide)	»	spectral
»	poly(propylene oxide)	»	»
»	poly(tetramethylene oxide)	»	»
»	poly(ethylene adipate)	»	»
Styrene	polydioxolan	»	spectral
Trioxan	dimethyl ethers of poly(oxymethylene glycol)	homopolymer	kinetic
Formaldehyde	ditto	»	»
Trioxan	poly(methyl methacrylate)	graft copolymer	spectral

TABLE 2. Preparation of block copolymers by the interaction of homopolymers [113].

Soluble polymer	Insoluble polymer
Polydioxolan	polyoxymethylene
Poly(tetramethylene oxide)	polyoxymethylene
Polydioxolan	poly-3,3-bischloromethyloxacyclobutane

Obviously, graft copolymers also can be synthesised by a similar procedure, if the functional group by which the chain is transferred is located in a side-branch of the homopolymer. Again, two methods of synthesis are possible — (1) the polymerisation of one monomer in a medium of the other homopolymer, and (2) reaction between the two homopolymers — results of the synthesis of graft polymers by the second method being listed in Table 3 [113].

It might be thought that block and graft copolymers are formed not as a result of CTF but by the copolymerisation of pairs of monomers produced during the establishment of equilibrium with an active polymer chain, which is itself formed by the action of the catalyst on the polymers. However, the results of the third experiment in Table 2 and of the experiments summarised in Table 3 show unambiguously that the block and graft copolymers were formed by a CTF reaction, since the starting homopolymers used could not act as monomer donors under the conditions of the experiments.

Thus, the synthesis of block and graft copolymers by the methods described is a rigorous chemical proof of the reality of CTF as an elementary act.

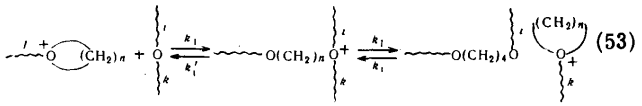
This act can be quite clearly identified even in homopolymerisation processes. A universal method of identification is the change in the molecular-weight distribution of the polymer during polymerisation. Some difficulties in the identification of this elementary act may arise when the polymerisation process is reversible, because under these conditions, too, the most probable molecular-weight distribution will establish itself in the system. These difficulties can be readily overcome by noting that in the case of reversible polymerisation the most probable distribution occurs only in the "live" part of the polymer.

An interesting effect is observed in the cationic polymerisation of oxygen-containing cyclic compounds. Thus, in the polymerisation of tetrahydrofuran [22] or trioxan [114], and perhaps also of other analogous compounds, a large increase in the viscosity of the reaction medium is found towards the end of the polymerisation process. Fig. 2 shows the variation in viscosity of the medium and in the extent of conversion as a function of time during polymerisation. This effect is not difficult to explain on the basis of CTF concepts.

TABLE 3. Preparation of graft copolymers by the interaction of homopolymers [113].

Soluble polymer	Insoluble polymer
Poly(butyl vinyl ether)	polyoxymethylene
Poly (butyl vinyl ether)	poly-3,3-bischloromethyloxacyclobutane

Thus, as was shown above (p. 310), the relative contribution of CTF to the polymerisation process should increase continuously as the reaction proceeds. Since a cyclic ether (acetal) is considerably more basic than a linear polyether, the rate of chain growth is higher, as a rule, than the rate of CTF. In this case the mechanism of CTF is complex, consisting of two consecutive acts: an active centre attacks the polymeric macromolecule with formation of an oxonium ion, and the resulting polymeric oxonium ion then decomposes:


(53)

The rate of the CTF process depends on the ratio of the constants for these elementary reactions: clearly, all the active centres should be in the form of polymeric oxonium ions towards the end of the reaction, so that the reaction medium consists of an aggregated system with labile bonds between polymer chains. Of course, this effect must cause a substantial increase in the viscosity of the medium. The viscosity of a system undergoing polymerisation drops to the normal value on treatment with a nucleophilic reagent[22], i.e. when the labile bonds are broken. The occurrence of this effect during homopolymerisation can itself be taken as evidence for CTF in the system under study.

Clear indications of interchain exchange and related interactions between a polymer chain and the starting materials or compounds of similar chemical nature have been obtained in the study of reactions leading to the formation of macromolecules by condensation polymerisation. As already pointed out, these reactions appear to proceed by a mechanism analogous to CTF. We shall call these reactions interchain exchange reactions in the case of condensation polymerisation.

Since fairly high temperatures are normally used for condensation polymerisation, the contribution of interchain exchange to the formation of macromolecules is considerably increased. We shall consider a few examples which illustrate interchain exchange processes occurring in condensation polymerisation reactions. These relate mainly to interchain exchange reactions of ester and amide groups.

We know from the theory of condensation polymerisation[3,4] that equivalent amounts of reactants are of great importance in the preparation of polymers of high molecular weight. Since functional groups of a single type do not interact, we can expect that a twofold excess, say, of one of the reactants will make it impossible to obtain a high-molecular-weight polymer: only low-molecular-weight reaction products should form in this case. Actually, however, it is possible to obtain products of fairly high molecular weight even in this case[115-117].

Thus, in the preparation of a polyester from a dicarboxylic acid and a diol with a twofold excess of one of the components, HOR'OOCR"COOR'OH or HOOCR"COOR'OOCR"COOH respectively are formed in the early stages of the reaction. Growth of the resulting "intermediates" becomes possible if exchange reactions by a transesterification mechanism (acidolysis or alcoholysis) take place:

$$2\,\mathrm{HOOCR''COOR'OOCR''COOH} \xrightleftharpoons{-R''(COOH)_2} \mathrm{HOOCR''[COOR'OOCR'']_{\frac{1}{2}}COOH},$$

$$2\,\mathrm{HOR'OOCR''COOR'OH} \xrightleftharpoons{-R'(OH)_2} \mathrm{HOR'[-OOCR''COOR'-]_2OH}. \quad (54)$$

The dicarboxylic acid or diol evolved is removed in a vacuum at a high temperature in order to displace the equilibrium. In practice, as a rule, a slight excess of diol is used, since this is the more volatile constituent and is more easily removed from the reaction medium.

The exchange interaction between amides and acids (or esters) can be used for the synthesis of polyamides.

Rafikov et al.[118] observed the formation of a polyamide from *NN'*-diacetylhexamethylenediamine and adipic acid:

$$n\mathrm{CH_3ONH(CH_2)_6NHCOCH_3} + n\mathrm{HOOC[CH_2]_4COOH} \rightleftarrows \mathrm{[-NH[CH_2]_6NHCO[CH_2]_4CO-]_n} + 2n\mathrm{CH_3COOH}. \quad (55)$$

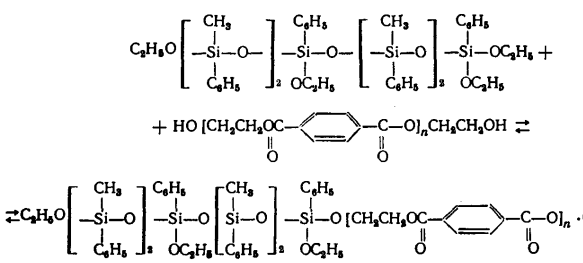
They also studied[118] the reaction between *NN'*-diacetylhexamethylenediamine and diethyl adipate. As before, the product of the reaction is polyhexamethyleneadipamide:

$$n\mathrm{CH_3CONH[CH_2]_6NHCOCH_3} + n\mathrm{C_2H_5OOC[CH_2]_4COOC_2H_5} \rightleftarrows \rightleftarrows \mathrm{[-NH[CH_2]_6NHCO(CH_2)_4CO-]_n} + 2n\mathrm{CH_3C(=O)OC_2H_5}. \quad (56)$$

Lastly, polyamides can be prepared by the exchange interaction of two diamides. Thus, Beste and Houtz[119] observed the formation of a polyamide from diacetylhexamethylenediamine and the diamide of sebacic acid:

$$n\mathrm{CH_3CONH[CH_2]_6HNCOCH_3} + n\mathrm{H_2NCO[CH_2]_8CONH_2} \rightleftarrows \rightleftarrows \mathrm{[-NH[CH_2]_6NHCO[CH_2]_8CO-]_n} + 2n\mathrm{CH_3CONH_2}. \quad (57)$$

The alcoholysis of polyesters has been suggested as a practical reaction for the regeneration of dimethyl terephthalate from poly(ethylene terephthalate) by treating the polymer with methanol[120]. Andrianov and his coworkers[121] demonstrated the interesting potential uses of alcoholysis in synthetic chemistry by preparing block and graft copolymers of poly(ethylene terephthalate) and polyorganosiloxanes:


(58)

The inclusion of ethoxy end-groups and side-groups in the polyorganosiloxane molecule leads to the formation of a mixed block-graft copolymer. The resulting copolymer has superior mechanical and dielectric properties and reasonably high thermal stability.

Kursanov et al.[122] demonstrated the occurrence of exchange interaction between two polyesters by an isotopic method. They studied the reaction between diethyl 2,3-dideuterosuccinate and poly(hexamethylene sebacate). The presence of deuterium in the polyester after reaction with the deuterated succinic ester is a proof of the occurrence of interchain exchange between polyester molecules.

A direct proof of ester exchange was given by Goodman and Nesbitt[123], who studied the interaction of poly(ethylene terephthalate) with tetramethylene dibenzoate and of poly(tetramethylene terephthalate) with ethylene dibenzoate. As a result of interchain exchange, they obtained ethylene and tetramethylene dibenzoates respectively.

The same workers showed that the cyclic trimer of ethylene terephthalate polymerises with formation of a linear polymer of high molecular weight. However, the reaction does not occur if the material is thoroughly dried. This suggests that the active initiator of the reaction is a hydroxy-acid, a hydrolysis product of the cyclic trimer. The mechanism of chain growth is an unusual trans-esterification reaction (acidolysis or alcoholysis) between the hydroxy-acid and the cyclic trimer.

The so-called hydrolytic polymerisation of lactams[4] involves a similar mechanism (transamidation). In general, from the point of view of the present Review, the polymerisation of any heterocycle can be treated as an exchange interaction irrespective of the type of active centre involved in the polymerisation.

Yet another general method of demonstrating the reality of interchain exchange reactions during condensation polymerisation depends on the formation of, say, a polyester from substances which contain neither free carboxyl nor free hydroxyl groups. Thus, a method of preparation of poly(ethylene terephthalate) from bis-2-acetoxyethyl terephthalate or bis-2-benzoyloxyethyl terephthalate has been described in the patent literature[124].

Several methods for identifying interchain exchange reactions are based on studies of the molecular weight, the molecular-weight distribution, or some other physical property of the products of condensation polymerisation[125]. Thus, when two samples of poly(decamethylene glycol) are mixed and heated[19], a fall in viscosity is observed: this is because the weight-average molecular weight decreases, although the number-average molecular weight remains constant under these conditions.

Using a very similar experimental approach, Rafikov et al.[126] separated by fractionation a narrow fraction of poly(ethylene adipate) from an unfractionated specimen. When this narrow fraction was heated in a sealed bulb at 170° the molecular-weight distribution became the same as in the original, unfractionated sample.

It is evident from the scheme discussed above that the acids and alcohols of low molecular weight generated by transesterification should lower the molecular weight of the polyester. Indeed, these phenomena have been thoroughly investigated in numerous publications by Korshak and his coworkers[125-136] and by others[69,137].

As in the case of polyesters, the exchange reactions accompanying the interaction between a polyamide and substance of a low molecular weight cause a lowering of the molecular weight of the former. Fig. 3 illustrates the results of the exchange reaction between polyhexamethyleneadipamide and adipic acid[128]. Similar results were obtained on reaction of this polymer with stearic acid[128] and of polycaprolactam with *p*-chlorobenzoic acid[138].

Korshak and Gribova[132] observed the aminolysis of polyurethane on heating it with aniline. They also showed that polyurethanes, like polyamides, can undergo, as well as aminolysis, exchange reactions with carboxylic acids, alcohols, and isocyanates[139].

A considerable lowering of molecular weight and softening temperature is observed when a polymer containing polysulphide links is treated with a thiol. Thus a liquid polymer of molecular weight ~ 5000 is formed when 5 mole % of butanethiol is added to an alkaline aqueous

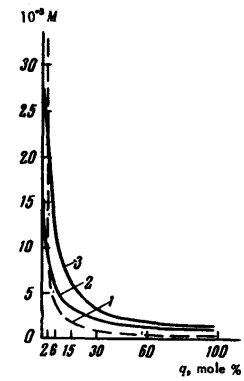


Fig. 3. Acidolysis of polyhexamethyleneadipamide by adipic acid (*q* mole %). Molecular weight:
1) calculated; 2) determined from viscosity;
3) determined from end-groups.

suspension of a macromolecular polysulphide[140]. Similar behaviour is observed with other substances which can denote alkyl sulphide ions, such as low-molecular-weight disulphides. Aromatic thiols, in particular thiophenols and mercaptobenzothiazole are effective donors[95]. Aliphatic thiols are less effective. Thiols with branched radicals have a very low activity[141] because of steric hindrance.

An interesting method, based on the change in physical properties of the resulting polymer, was used by Korshak and his coworkers[142] to demonstrate the occurrence of interchain exchange in condensation polymerisation. A polyamidoester of the composition

$$[-OCH_2CH_2NHCO[CH_2]_8CO-]_n,$$

(I)

was obtained by the condensation polymerisation of 2-aminoethanol with sebacic acid. Condensation polymerisation of *NN'*-bis-2-hydroxyethylsebacamide with sebacic acid was also carried out. The product in this case should have had the structure

$$[-OCH_2CH_2NHCO[CH_2]_8CONHCH_2CH_2OCO[CH_2]_8CO-]_n.$$

(II)

The two polymers were examined by electron diffraction, and found to have exactly the same identity period of 17 Å. This corresponds to the polyamidoester structure given by formula (I), whence we may conclude that polymer (II) has been converted into polymer (I) as a result of interchain exchange.

Kresse[143] used the lowering of the melting point of a copolyester (as compared with that of a mechanical mixture of the two separate polyesters) to detect interchain exchange. In exactly the same way, a copolymer was prepared from a mixture of three polyamides — poly(hexamethyleneazelaamide), polyhexamethyleneadipamide, and polycaprolactam — formation of the copolymer being demonstrated by monitoring the gradual fall in the melting point of the mixture of polyamides on heating[144]. The melting point continues to change until an equilibrium distribution of monomer units is established in the copolymer, as is clearly shown in Fig. 4, which is a plot of the flow temperature of the three-component system as a function of time of heating[144]. The authors also suggested[144] that

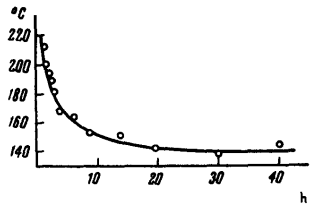


Fig. 4. Variation of the flow temperature of polyhexamethyleneazelaamide–polyhexamethyleneadipamide–polycaprolactam copolymers as a function of time of heating of the homopolymers [144].

the stability of solution of the resulting products can be used to characterise structural changes in the polyamide macromolecules during heating of the homopolyamides.

Technically valuable products have been obtained through the preparation of a copolyamide by heating a mixture of the two homopolyamides polyhexamethyleneadipamide and polycaprolactam [145,146]. It is interesting to compare the difference in melting point between copolymers of a given composition prepared either from the corresponding monomers or from the homopolymers [146,147]. As can be seen from Fig. 5, the melting points of the copolymers differ quite markedly, indicating that the distribution of monomer units is different in the two cases.

Results in good qualitative agreement with this conclusion have been obtained [148] from a study of the tensile strength of mixtures of homopolyamides as a function of time of heating, i.e. essentially as a function of the extent of interchain exchange. As shown in Fig. 6, progress of the reaction is accompanied by a gradual decrease in the tensile strength of the copolyamide. On the basis of the mechanism suggested above for CTF, we may assume that the high initial strength of the copolyamide stems from the large blocks formed in the block copolymer in the initial stages of the reaction; as the reaction proceeds, these blocks are broken up, and this appears to lower the tensile strength of the copolymer.

Thus, as shown by Korshak and his coworkers [149], a block copolymer is formed rapidly on heating mixtures of homopolyamides, the size of the blocks decreasing as interchain exchange proceeds. The system ultimately reaches an equilibrium state characterised by the appropriate distribution of monomer units in the copolymer. The

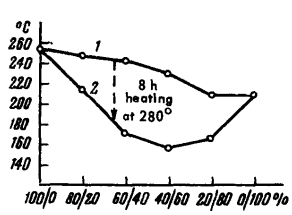


Fig. 5. Variation with composition in melting points of:
1) mixtures of polyhexamethyleneadipamide and polycaprolactam; 2) copolyamides.

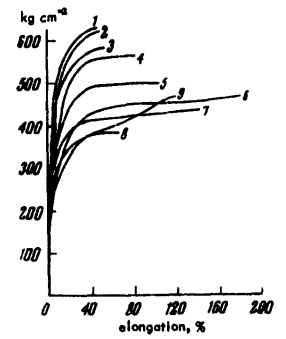


Fig. 6. Variation of the tensile strength of a mixture of polyhexamethyleneadipamide and polycaprolactam with time of heating (h):
1) 0.5; 2) 1; 3) 1.5; 4) 2; 5) 4; 6) 6; 7) 12; 8) 20; 9) 30.

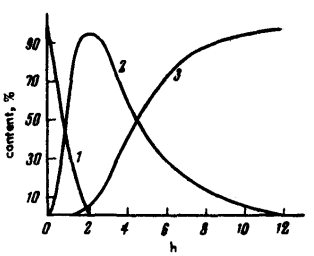


Fig. 7. Change in composition of a mixture of polyamides with heating [148]:
1) content of homopolymers; 2) content of block copolymers; 3) content of copolyamide.

change in composition of a mixture of polyamides is shown in Fig. 7.[148]

The progress of interchain exchange between two homopolymers can be followed by choosing a solvent in which one of the homopolyamides is insoluble. Thus it was found [149] in a study of the reaction between polyhexamethyleneadipamide and polyhexamethyleneisophthalamide that the latter polymer is insoluble in formic acid. When this mixture was heated, the usual fall in melting point was observed, and at the same time the amount of insoluble polyhexamethyleneisophthalamide decreased with time, as shown in Fig. 8. It is evident from these results that only a relatively crude indication of the extent of interchain exchange can be obtained from the change in melting point of a mixture of polymers, particularly in the initial stages, when the block copolymers formed consist of large blocks and have melting points little different from that of a mechanical mixture of the homopolymers.

Unambiguous evidence for the presence of interchain exchange was obtained in the study of naturally occurring molecules containing peptide links. A characteristic feature of these reactions is the fact that they proceed in aqueous media, where the peptide links can undergo hydrolytic reactions. These reactions occur under the influence of enzymes.

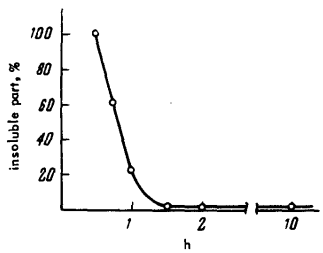
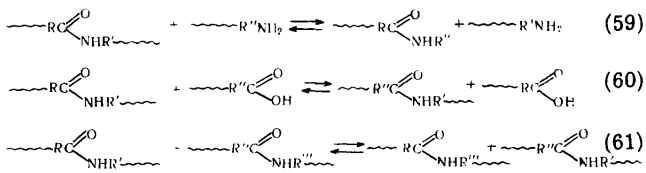


Fig. 8. Change in the relative amount of formic-acid-insoluble material in a polyhexamethylene-adipamide–polyhexamethyleneisophthalamide melt as a function of time of heating [149].

It was shown that various proteolytic enzymes, highly specific in action, can induce transpeptidation reactions as well as hydrolysis, whilst displaying their individual specificity. The term transpeptidation reaction refers to an interchain exchange reaction involving peptide links.

The discovery of transpeptidation is of the greatest interest, because these reactions can play an important role in the synthesis of proteins. In general, transpeptidation reactions can be represented by the following schemes



The earliest report of the possibility of reactions of this type is due to Bergmann [150], who discovered the reaction

$$\text{Hippuroylamine} + \text{Aniline} \xrightarrow{\text{papain}} \text{Hippuroylaniline} + NH_3. \qquad (62)$$

It may be thought that the hippuroylaniline was formed by initial hydrolysis of the hippuroylamine followed by reaction between the free hippuric acid and aniline. However, special experiments showed that the rate of reaction (62) is greater than that of the analogous reaction in which hippuric acid was used as the substrate [150]. Therefore, hippuric acid is not an intermediate in this process. In this way a new type of reaction brought about by proteolytic enzymes — exchange interaction — was postulated.

These results were subsequently confirmed by a series of investigations by Fruton and his coworkers [151-153], who showed that papain, activated by cysteine, catalyses the replacement of the amide nitrogen in *N*-benzoylglycinamide or benzyloxycarbonyl-*L*-methioninamide by ^{15}N, introduced in the form of $^{15}NH_4^+$. Exchange of the amide group can occur also when the amide reacts with hydroxylamine, leading to the formation of the corresponding hydroxamic acid [152,153]. Preliminary hydrolysis of the amide, followed by reaction between the free hydroxyl and the hydroxylamine, is out of the question, since it has been shown experimentally that free amino-acids do not form hydroxamic acids with hydroxylamine to a significant extent. Similar results were obtained when different enzyme systems — ficin and chymotrypsin [154,155], and also cathepsin [152,155] — were used as exchange activators.

Many investigations showed that the ability to undergo exchange is an almost universal property of the amides of various amino-acids. The amide group has a general tendency to exchange with various compounds, in particular with hydroxylamine and ammonia, and the latter can be used in the form of nitrogen-labelled ammonium salts. The exchange reaction takes place in the presence of enzymes of vegetable [155,156] and animal [157,158] origin, and of bacteria [159,160].

Exchange of the amide group has been used in synthetic chemistry to build up polypeptide chains. It has been shown [161] that benzoyltyrosylglycinamide is formed when benzoyltyrosinamide reacts with glycinamide in the presence of chymotrypsin. In a similar way, benzyloxycarbonylglycyltyrosinamide can be obtained from benzyloxycarbonylglycinamide and tyrosyinamide in the presence of papain. The action of cathepsin on glycylphenylalaninamide was shown to yield a whole range of polypeptides of different molecular weights. Polypeptides are formed also from glycyltyrosinamide, alanylphenylalaninamide, and other amides [162,163] in the presence of this enzyme. Experiments by Orekhovich and Kaganova [164] provided additional suuport for the participation of amides in the biosynthesis of peptide links. By treating a tyrosine ester with glutamine or asparagine in the presence of crystalline chymotrypsin these workers obtained a peptide containing a tyrosine residue and glutamic or aspartic acid. If the amides are replaced by aspartic or glutamic acid, formation of a dipeptide does not occur. Many reactions of this type have been reported [165-173] and systematised in a number of reviews and monographs [53,86,174-180]. These include, for example, the formation of plasteins [169-173], which are insoluble peptides with molecular weights up to 400 000.

The examples given above clearly show that transpeptidation reactions are undoubtedly involved in the biosynthesis of peptide links, but their exact role in the general process of protein biosynthesis is still far from clear. Systematic quantitative experiments may, perhaps, solve this problem. This work should also go some way towards the solution of two other important aspects of the general problem of the biosynthesis of proteins: the influence of transpeptidation reactions on the sequence of amino-acid residues in the protein molecule and also the importance of these exchange interactions in the dynamic state of proteins, peptides, and amino-acids in the living organism.

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It is evident from what has been said above that reactions involving chain transfer with fission are of common occurrence in processes giving rise to the formation of heterochain polymers. Tney play a most important role in the formation of macromolecules, and they determine the properties of the resulting polymer to quite a large extent. Thus, they open up wide prospects for the controlled modification of heterochain polymers.

By including CTF among the primary steps in polymerisation, we gain a much deeper understanding of the thermodynamic and kinetic peculiarities of this process. Furthermore, many experimental facts could not be interpreted otherwise than in terms of CTF.

The discovery of transpeptidation justifies the hypothesis that interchain exchange reactions play an essential role in the biosynthesis of proteins.

The present Review will not have been written in vain if it can focus attention on the importance of CTF in processes leading to the formation of heterochain polymers, and on its potentialities in synthetic chemistry.

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CHEMICAL REACTIONS AT TEMPERATURES CLOSE TO 77°K

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I. INTRODUCTION

A new branch of chemistry, the study of chemical processes at low temperatures, close to the boiling point of liquid nitrogen, arose in recent years and has rapidly developed. Comparatively recently chemical reactions at low temperatures appeared to be unlikely. This view arose from the fact that the Arrhenius factor, which takes into account the necessity to overcome the activation barrier, increases sharply as the temperature is reduced. Furthermore, at low temperatures most substances are in the solid state where the mobility of the species is extremely low and molecular collision necessary for reaction is difficult to achieve.

Initially, the attention of chemists, who began to work at low temperatures, was drawn mainly to the problem of formation and stabilisation of radicals. Gradually the range of problems investigated widened and at present the study of the fundamental steps in the reaction of various species in the solid phase at low temperatures is one of the central problems of modern chemical kinetics. N.N.Semenov and his school and many other Soviet scientists have made a major contribution to the development of these studies.

The present review deals with certain results of studies on chemical reactions at low temperatures obtained in the Department of Chemical Kinetics at Moscow State University, directed by N.N.Semenov. In the course of these investigations the phenomenon of a spontaneous, explosive course of many chemical reactions at temperatures close to the boiling point of nitrogen and the effect of phase transitions on chemical processes were discovered, the possibility of chain reactions in the solid phase at this temperature was demonstrated, and the special role of unstable molecular complexes of the donor–acceptor type and their aggregates in low-temperature chemical reactions has been observed.

The Review consists of three principal parts. In the first section certain problems of the preparation and reactions of radicals in the solid phase are considered. The second section deals with the characteristic features of

low-temperature chain reactions — photochemical hydrobromination of certain olefins and halogeno-olefins. In the third section a wide variety of chemical reactions occurring at low temperatures are described, and the peculiarities of the mechanism of fast spontaneous chemical reactions are examined, using the halogenation of olefins as an example.

II. PREPARATION AND REACTIONS OF RADICALS AT LOW TEMPERATURES

The problems of the formation, stabilisation, and destruction of radicals at low temperatures have been discussed in many reviews and monographs [1-5]. In order to elucidate certain general features of these processes, the mechanism and characteristic features of the photolysis of frozen aqueous solutions of hydrogen peroxide have been investigated in the Department of Chemical Kinetics of Moscow State University for many years [6-10]. The data obtained permit a deeper understanding of the specific features of the photolysis and radiolysis of aqueous solutions of other substances and suggest an approach to the problem of the detailed role of structured water in biological systems.

Hydrogen peroxide was the first substance for which the special role of phase transitions and chemical reactions at low temperatures was discovered by an electron spin resonance (ESR) study of the destruction of H_3O_2 radicals [6-8]. Depending on the rate of freezing, 25% aqueous solutions of hydrogen peroxide can be obtained at 77°K in a crystalline or vitreous state. When such specimens are irradiated at 77°K with ultraviolet light from a mercury quartz lamp, ESR measurements reveal the presence of HO_2 radicals which have a characteristic asymmetric spectrum and are formed in the reactions

$$H_2O_2 + h\nu \rightarrow 2\,OH,$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2.$$

In vitreous specimens the destruction of radicals does not begin until 143°K and the radicals are completely eliminated by 158°K. In 25% hydrogen peroxide solutions this is the temperature of the glass–crystal phase transition. The destruction of radicals is associated with the fact that at the instant of phase transition changes in structure, leading to considerable mobility of the molecules, usually occur. For example in hydrogen peroxide solutions in the temperature range 153–158°K the viscosity of the glass increases so much at the instant of phase transition that a thermocouple inserted into the specimen may be withdrawn [with difficulty (Ed. of Translation)].

In crystalline specimens radicals are not destroyed at 158°K. When the specimens are irradiated with ultraviolet light below the phase-transition temperature, for example at 163°K, it is again possible to obtain a considerable concentration of HO_2 radicals. On further increase in temperature, destruction of radicals in a characteristic stepwise manner was observed (Fig. 1). The data in Fig. 1 show that in the temperature range 163–183°K a definite proportion of radicals are destroyed at each discrete temperature. The radicals are completely eliminated only at 220°K at the instant of fusion of the eutectic mixture.

A similar process involving the destruction of radicals at the instant of phase transition was also observed at 103°K in the photolysis of hydrogen sulphide frozen at 77°K. [7] Subsequently studies of the role of phase transitions in radical destruction processes were developed

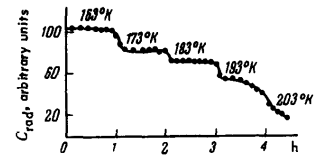


Fig. 1. Effect of temperature on the recombination of HO_2 radicals.

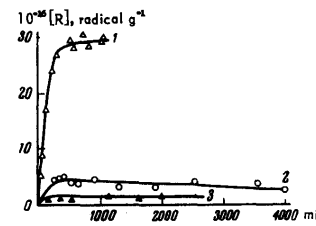


Fig. 2. Accumulation of radicals in dilute hydrogen peroxide solutions at 77°K; concentration of hydrogen peroxide (M): 1) 2×10^{-1}; 2) 4.3×10^{-2}; 3) 4.1×10^{-3}.

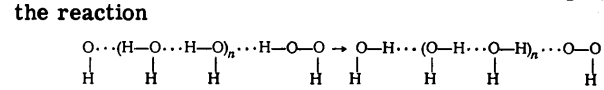
extensively in the Institute of Chemical Physics of the USSR Academy of Sciences and were summarised in Semenov's report to the Eighteenth Congress of the International Union of Theoretical and Applied Chemistry [1].

In recent years many interesting features have been observed in the photolysis of very dilute aqueous solutions of hydrogen peroxide with and without various additives. Fig. 2 shows the variation of the yield of radicals with irradiation time for various hydrogen peroxide concentrations. For the concentration 4×10^{-3} M, the ESR spectrum observed results from the superposition of the spectra of OH and HO_2 radicals. As irradiation is continued, the amount of the HO_2 admixture falls. For the solution in which the concentration is 4×10^{-2} M, the HO_2 spectrum is first observed and then the spectrum of hydroxyl radicals begins to be superimposed. The above changes in the composition of radicals are probably associated with the disappearance of the peroxide and the photolysis of HO_2 in the reaction

$$HO_2 + h\nu \rightarrow H + O_2.$$

The possibility of the photolysis at 77°K of HO_2 radicals is indicated by data obtained in a comparative study of the photolysis and radiolysis of 55% hydrogen peroxide solutions in water [9]. The concentration of HO_2 radicals during radiolysis is higher than during photolysis. When specimens subjected to preliminary irradiation from cobalt-60 were illuminated with ultraviolet light, the concentration of HO_2 radicals fell and approached the value obtained during photolysis alone. The decrease in the line-width of the ESR spectrum, which is observed on increase in the concentration of radicals, is also evidence in favour of the reaction $HO_2 + h\nu \rightarrow H + O_2$. In concentrated solutions the HO_2 radicals formed are initially distributed in pairs. With increase in the duration of illumination, part of the HO_2 radicals are photolysed and their distribution approaches statistical uniformity, which is reflected in a narrowing of the ESR spectral line.

Since diffusion of OH radicals in ice at 77°K is unlikely (OH radicals are stabilised), in order to account for the occurrence of the reaction $OH + H_2O_2 \rightarrow H_2O + HO_2$ at concentrations 10^{-3} M (55 000 H_2O molecules per H_2O_2 molecule), the hypothesis was put forward that there is a possibility of a non-diffusional bond transfer along the system of hydrogen bonds[10]. If the three-dimensional distribution of H_2O_2 molecules in a frozen dilute solution is statistically uniform and the formation of HO_2 radicals occurs in consequence of non-diffusional bond transfer, for example, by the reaction



then any significant breakdown of the structure of hydrogen bonds should result in bond transfer over much smaller distances. One would then expect that OH radicals would be stabilised at H_2O_2 concentrations in excess of 2×10^{-2} M. To check this hypothesis, we carried out experiments on the photolysis of a rapidly frozen solution of hydrogen peroxide (0.16 M) in 8 M sodium perchlorate. This solution froze into a transparent glass in which the hydrogen bond structure may be appreciably degraded. When such solutions are illuminated with ultraviolet light, the ESR spectrum of the OH radical is obtained. The initial rate of formation of radicals is smaller by a factor of approximately 100 than in the photolysis of aqueous solutions. In solutions of similar concentration but without sodium perchlorate only HO_2 radicals are observed. Thus the results of the photolysis of hydrogen peroxide in sodium perchlorate solutions appear to confirm the validity of the earlier hypothesis of non-diffusional bond transfer along the hydrogen bond system in ice.

In the photolysis of dilute aqueous hydrogen peroxide solutions the initial rate w_0 of formation of HO_2 radicals varies linearly with the concentration of hydrogen peroxide. This means that almost all the OH radicals formed in the primary step enter into the reaction $OH + H_2O_2 \rightarrow H_2O + HO_2$. However, in the photolysis of frozen hydrogen peroxide solutions to which isopropanol, which does not absorb light in the wavelength range investigated, had been added, the initial rate of formation of radicals is higher by a factor of fifty. It is difficult to explain this phenomenon. Possibly at low temperatures apart from the reactions

$$H_2O_2 + h\nu \rightarrow 2\,OH,$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2,$$

the following reaction may occur in the given case:

$$OH + HO \rightarrow H_2O + O.$$

Oxygen atoms are not detected at low temperatures by the ESR method[4]. In this case in the presence of the alcohol in the system of the two competing reactions

$$O + H_2O_2 \rightarrow OH + HO_2 \quad (\text{or } O + H_2O_2 \rightarrow O_2 + H_2O)$$

and

$$O + \text{iso-}C_3H_7OH \rightarrow OH + CH_3{-}\dot{C}(OH){-}CH_3,$$

the second predominates, which results in an increased yield of stabilised radicals.

Another explanation of the observed peculiarities of the photolysis of dilute hydrogen peroxide solutions can be obtained on the assumption that on rapid freezing of such solutions hydrogen peroxide may be precipitated as a separate phase. Differential thermography showed that, in rapidly frozen solutions in which the hydrogen peroxide concentration is greater than 0.4 M, the peroxide is indeed evolved as a separate phase. In such a case the difference in the rate of accumulation of radicals when sodium perchlorate and the alcohol are added can probably be accounted for by the cage effect. It is a maximum for sodium perchlorate and a minimum for the alcohol. It must also be postulated that the alcohol is incorporated into the peroxide crystals.

In conclusion it must be emphasised that the study of the photolysis of very dilute frozen aqueous solutions of hydrogen peroxide in the presence of additives made it possible to elucidate a number of new interesting facts which, however, require further study. In the Department of Chemical Kinetics at Moscow State University extensive studies are being made on the photochemical and non-photochemical reactions with participation of halogens and hydrogen halides. To obtain more detailed data on the possibility of the occurrence at low temperatures of reactions of the type $X + RH \rightarrow R + HX$ (X = halogen atom) and to elucidate the characteristic features of the photolysis of binary mixtures of halogens with various organic compounds, a study was made of the formation of radicals at 77°K when mixtures of bromine and chlorine with certain hydrocarbons and alcohols are irradiated with ultraviolet light[11,12]. Compounds with weak C–H bonds and readily undergoing vitrification at low temperatures were mainly investigated. It was assumed that both these factors facilitate the formation of radicals.

The choice of alcohols was also associated with the familiar fact of the formation of molecular complexes with halogens by oxygen-containing compounds[13]. The aim was to elucidate the role of such compounds in the formation of radicals at low temperatures.

In the photolysis experiments the halogen and the organic compound were mixed in specified proportions in a vacuum apparatus. The mixture was frozen with liquid nitrogen in the tip of a quartz tube and illuminated at 77°K with filtered ultraviolet light from a PRK-7 lamp for a specified period. The specimen was then transferred to the resonator of electron spin resonance apparatus and the ESR spectra were recorded at 77°K.

After frozen mixtures of chlorine with isopentane, pentane, iso-octane, and cyclohexane had been illuminated with ultraviolet light at a wavelength $\lambda > 280$ mμm, ESR spectra revealed the presence of radicals. The experimental conditions and the results are presented in Table 1.

Fig. 3 shows as an example the ESR spectra obtained for mixtures of chlorine with isopentane and cyclohexane. The number of hyperfine structure components and their splitting in these spectra are consistent with those described in the literature[14,15] and are evidently due to alkyl radicals of the type $(CH_3)_2{-}\dot{C}{-}CH_2{-}CH_3$ and C_6H_{11}. It should be noted that we were the first to observe at 77°K the additional splitting of each of the six components in the spectrum of the cyclohexyl radical due to β-protons lying in a plane different from the one containing the protons responsible for the main spectrum. Probably the presence of chlorine (m.p. 172°K) makes the system more rigid. The hydrocarbons used in the experiments are transparent to light at a wavelength of 280 mμm. Solid chlorine absorbs light and radicals are formed as a result of the following reactions:

$$Cl_2 + h\nu \rightarrow 2\,Cl,$$

$$Cl + RH \rightarrow HCl + R.$$

TABLE 1. Results of the photolysis of hydrocarbons in the presence of chlorine and bromine at 77°K.

Experimental conditions			Results		
halogen and its amount in mixture, moles	hydrocarbon : halogen ratio	duration of irradiation, min	state of specimen	concentration of radicals, radical g^{-1}	characteristics of ESR spectrum
Iso-octane					
Chlorine 3.9×10^{-4}	1 : 1	60	vitreous	2.1×10^{18}	11 hyperfine structure lines, $\Delta H = 13$ oersteds
Chlorine 7.4×10^{-5}	5 : 1	60	vitreous	5.0×10^{18}	ditto
Chlorine 3.9×10^{-5}	10 : 1	60	vitreous	6.7×10^{16}	
Bromine 3.9×10^{-4}	1 : 1	300	vitreous		radicals not detected
Isopentane					
Chlorine 3.9×10^{-5}	10 : 1	180	vitreous	5.6×10^{17}	8 hyperfine structure lines, $\Delta H = 24$ oersteds
Bromine 3.9×10^{-5}	10 : 1	180	vitreous		radicals not detected
Pentane					
Chlorine 3.9×10^{-5}	10 : 1	180	vitreous	3.0×10^{16}	hyperfine structure poorly resolved
Bromine 3.9×10^{-5}	10 : 1	180	vitreous		radicals not detected
Cyclohexane					
Chlorine 3.9×10^{-5}	10 : 1	180	crystalline	5.9×10^{16}	6 hyperfine structure lines with additional splitting
Bromine 3.9×10^{-5}	10 : 1	300	crystalline		radicals not detected

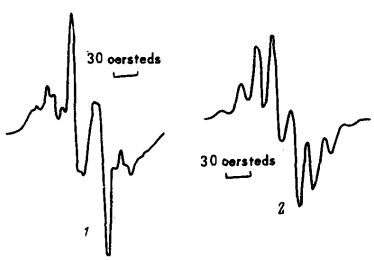


Fig. 3. ESR spectra of the radicals formed on illumination of chlorine–hydrocarbon mixtures at 77°K: 1) in cyclohexane; 2) in isopentane.

The data in Table 1 show that the yield of radicals depends on the amount of chlorine added, the number of radicals formed decreasing as the concentration of chlorine is reduced. This variation confirms the above mechanism for the formation of radicals. The yield of radicals is higher, the weaker is the C–H bond in the hydrocarbon.

It is interesting that in the photolysis of mixtures of hydrocarbons with bromine radical formation is not observed. The absence of radicals in this case is probably due to the high energy required for the reaction

$$Br + RH \rightarrow HBr + R.$$

Radical reactions with participation of bromine atoms are as a rule markedly endothermic [16], and therefore proceed with difficulty at low temperatures.

In contrast to hydrocarbons, in alcohols (methanol, ethanol, isopropanol) radicals were observed not only on addition of chlorine but also in the presence of added bromine. The mixtures were illuminated with light at a wavelength $\lambda > 280$ mμm. When the wavelength was changed from $\lambda < 280$ [sic] to $\lambda > 320$ mμm, radicals were not observed. The photolysis of alcohols with added halogens results in a complex mixture of radicals. This is because a number of secondary reactions involving the photolysis of the radicals occur during the irradiation. In their main outline these processes are similar to those observed in the photolysis of alcohols with added hydrogen peroxide. The radical reactions in methanol and ethanol during irradiation have been investigated in detail by Fok in the Department of Chemical Kinetics at Moscow State University [17,18]. In isopropanol secondary radical reactions are not observed and therefore the isopropanol–halogen system was chosen to investigate the kinetics of the accumulation of isopropanol radicals as a function of the amount of bromine or chlorine added. Experiments were made with alcohol : halogen = 10 : 1, 100 : 1, 1000 : 1, 10 000 : 1. The results obtained are presented in Table 2 and in Fig. 4.

In contrast to hydrocarbons, with alcohols there is a complex relation between the limiting yield of radicals and the amount of halogen added. The data in Fig. 4 show that the maximum yield of isopropanol radicals occurs at an alcohol : halogen ratio of 100 : 1. The initial rate of formation of radicals is also a maximum at this ratio. The occurrence of this relation and the very fact that considerable concentrations of radicals are obtained in the presence of bromine probably indicate that the mechanism of radical formation in alcohol–halogen systems is different from that in hydrocarbon–halogen mixtures.

The dissociation energies of C–H bonds in alcohols are comparable to the dissociation energies of similar bonds in branched-chain paraffins [19]. The activation energy for the reaction Br + ROH → RCHOH + HBr is about 9 kcal $mole^{-1}$

TABLE 2. Photolysis of isopropanol in the presence of added chlorine and bromine at 77°K.

Experimental conditions			Results	
halogen and its amount, moles	alcohol : halogen ratio*	duration of irradiation, min	radical concentration, radical g^{-1}	characteristics of ESR spectra
Chlorine 6.5×10^{-8}	10 : 1	720	4.5×10^{17}	in all cases the isopropanol radical was detected, with six lines at 77°K and seven lines at 110°K, $\Delta H = 21.4$ oersteds
Chlorine 6.5×10^{-6}	100 : 1	720	1.1×10^{18}	
Chlorine 6.5×10^{-7}	1000 : 1	720	5.3×10^{16}	
Chlorine 6.5×10^{-8}	10 000 : 1	720	1.4×10^{16}	
Bromine 6.5×10^{-8}	10 : 1	720	3.6×10^{16}	
Bromine 6.6×10^{-6}	100 : 1	720	7.6×10^{17}	
Bromine 6.5×10^{-7}	1000 : 1	600	6.9×10^{16}	
Bromine 6.5×10^{-8}	10 000 : 1	720	1.9×10^{16}	

* For the alcohol : halogen ratios indicated in the table, satisfactory vitreous specimens were obtained at low temperatures.

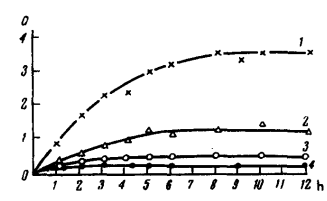


Fig. 4. Curves for the accumulation of isopropanol radicals on illumination of the bromine–isopropanol system at 77°K; alcohol : bromine ratio: 1) 100 : 1; 2) 1000 : 1; 3) 10 : 1; 4) 10 000 : 1; C is the concentration of radicals in arbitrary units.

in the case of methanol[20]. As a result of this high activation energy, direct removal of hydrogen from the alcohol molecule by a bromine atom is unlikely at low temperatures. In our view in alcohol–halogen systems radicals are formed under the action of light as a result of the condensation of the molecular charge-transfer complexes (formed during the process), which significantly alters the absorption spectrum of the system. The existence of such complexes at low temperatures is indicated by literature data. For example, Groth and Hassel established that bromine and methanol form a 2 : 1 compound which melts at 213°K.[21] X-Ray diffraction analysis showed that the alcohol molecules are linked into chains by hydrogen bonds and bromine forms cross-links between the chains.

Additional confirmation of the existence of molecular compounds in frozen mixtures of isopropanol with bromine and chlorine was obtained by the present author by a spectrophotometric method. In order to obtain the ultraviolet spectra, the halogen, alcohol, and their mixtures were frozen in the form of thin films on to a quartz plate cooled with liquid nitrogen. Fig. 5 shows as an example the absorption spectra of isopropanol, bromine, and their mixture. It is seen that, when bromine and alcohol are frozen out simultaneously, there is a marked displacement of the bromine band in the region of 384 mμm towards shorter wavelengths and a new band appears in the region of 232 mμm. Such changes in ultraviolet spectra are characteristic of charge-transfer complexes[13]. The displacement of the absorption band towards short wavelengths associated with complex formation explains the finding noted above that radicals are not formed when the wavelength of the light irradiating the mixture is changed from $\lambda > 280$ to $\lambda > 320$ mμm.

One of the possible modes of formation of isopropanol radicals consists in the excitation of the complex on absorption of light and electron transfer from the alcohol oxygen atom to bromine. Such transfer may result in the formation of the radical $CH_3-\overset{\displaystyle H}{\underset{\displaystyle O^{\cdot}}{\overset{|}{\underset{|}{C}}}}-CH_3$ which under the action of light rapidly isomerises to the isopropanol radical $CH_3-\overset{\displaystyle \cdot}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-CH_3$, whose ESR spectrum has a seven-component hyperfine structure.

The formation of molecular charge-transfer complexes is determined to a first approximation[13,19] by the ionisation potential of the donor and the electron affinity of the acceptor. Since the difference between the electron affinities of bromine and chlorine is small (1.3 and 1.2 eV)[22] and radicals are formed in alcohols as a result of the photolysis of molecular complexes, their yield should depend only slightly on the nature of the added halogen. The data in Table 2 confirm this conclusion. In contrast to alcohols, hydrocarbons do not form molecular complexes with halogens. Here the formation of radicals depends mainly on the energy relations of secondary reactions and also on the mobility of the halogen atoms, which is determined by their size and the excess energy which they receive during photolysis. The formation of radicals in mixtures of alcohols with halogens occurs in a fundamental step which consists in the photolysis of an intermediate which is stable only at low temperatures. Radicals are formed as a result of electron transfer, and the cage effect is then probably excluded. The suggested mechanism

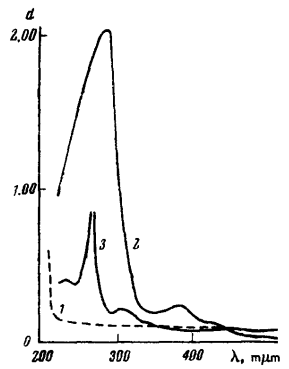


Fig. 5. Ultraviolet absorption spectra at 77°K:
1) isopropanol; 2) bromine; 3) bromine–alcohol mixture.

differs from those described in the literature for the photolysis of frozen alcohols[4,17,23]. The mechanism of radical formation by the photolysis of molecular complexes is probably common to all systems in which donor–acceptor interaction is possible.

The problem of reactions with participation of radicals during the formation of the latter is of fundamental importance both for the problem of the stabilisation and accumulation of radicals and for the possibility of carrying out various low-temperature reactions. For the solution of these problems, the author has used simultaneously electron spin resonance and gas–liquid chromatography. The results obtained in the study of the radiolysis of isopropanol will be given as an example.

The alcohol, purified from traces of acetone on a semi-preparative chromatograph, was freed from dissolved air and irradiated with X-rays for 3 h at 77°K and 90°K. The irradiated specimens were then transferred to the resonant cavity of the ESR apparatus for the determination of the concentration of the isopropanol radicals formed. After the ESR spectra had been measured, the irradiated alcohol specimens were heated to room temperature and analysed. The products were determined with a gas–liquid panchromatograph fitted with a macro-argon detector. The stationary phase was poly(ethylene glycol) with a molecular weight of 400. A large amount of acetone was detected in the reaction products. Preliminary calibration of the detector with artificial mixtures made it possible to make quantitative measurements. The results are presented in Table 3.

The isopropanol radicals obtained in the radiolysis can probably recombine on heating:

$$CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}-CH_3 + CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}-CH_3 \rightarrow CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}-\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}-CH_3,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3\ CH_3$$

with formation of pinacol, and disproportionate

$$2\,CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}-CH_3 \rightarrow CH_3-\overset{\displaystyle O}{\overset{\|}{\underset{|}{C}}}-CH_3 + CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{|}{CH}}}-CH_3,$$

with formation of acetone and isopropanol. Pinacol could not be detected in the reaction products. Probably its amount is smaller than 10^{-8} g per microlitre, the minimum

TABLE 3. Amount of radicals and acetone in irradiated isopropanol.

Temperature, °K	Amount of radicals in 1 μl, g	Amount of acetone Q_T from radicals in 1 μl, g	Amount of acetone Q_A found by analysis in 1 μl, g	Difference $Q_A - Q_T$ in 1 μl, g
77	$1.1 \cdot 10^{15}$	$5.3 \cdot 10^{-8}$	$2.2 \cdot 10^{-7}$	$17 \cdot 10^{-8}$
90	$1.6 \cdot 10^{15}$	$7.7 \cdot 10^{-8}$	$2.7 \cdot 10^{-7}$	$19.3 \cdot 10^{-8}$

quantity of pinacol which could be detected in the artificial mixtures. Thus the data in Table 3 show that, when the frozen alcohol is heated, the isopropanol radicals mainly disproportionate. This is consistent with the known fact that disproportionation reactions of free radicals require a smaller activation energy than their recombination[24].

Comparison of the data in columns 3 and 4 of Table 3 shows that a large part of the acetone forms during radiolysis in the solid phase. Under the present experimental conditions the yield of radicals varies linearly with dose. Assuming that acetone forms in the solid phase as a result of radical disproportionation and that its yield follows a similar linear relation, it is possible to estimate from the data in Table 3 by the Arrhenius equation the energy of disproportionation of isopropanol radicals as 150 cal mole^{-1}. This value is consistent with the literature data for similar reactions[24] and shows that the simultaneous application of ESR and gas chromatographic methods in combination with low temperatures opens up great possibilities for quantitative investigations of fundamental reactions.

III. CHAIN REACTIONS IN THE SOLID PHASE AT TEMPERATURES CLOSE TO 77°K

Chain reactions with participation of free radicals occur widely in both gas and liquid phases[16,25]. The occurrence of such reactions at low temperatures is of considerable theoretical and practical interest. The possibility of accumulation at the boiling point of liquid nitrogen of considerable non-equilibrium concentrations of radicals and the appearance of stable products under these conditions suggested that chain reactions can also occur in the solid phase. It might have been expected that such reactions would proceed most readily upon irradiation.

We chose for investigation the photochemical hydrobromination of olefins and halogeno-olefins. In gas and liquid phases these reactions occur under the action of light and are typical chain reactions with a chain length of thousands of units[16]. It has been established that photochemical hydrobromination of olefins in the solid phase at 77° proceeds vigorously and explosively[26-28]. The products are alkyl bromides.

The experiments were made in a vacuum apparatus. A mixture of hydrogen bromide and the appropriate olefin was condensed in the reaction vessel, cooled with liquid nitrogen, and then illuminated for a specified period. The reaction was followed by differential thermal analysis. The extent of reaction was usually determined from the change in pressure after heating the irradiated mixture to room temperature. The extent of reaction increased with the duration of irradiation at 77°K. A number of special experiments established that the reaction is initiated by bromine atoms which are formed on photolysis of hydrogen bromide[26]. The formation of radicals during the preliminary illumination of mixtures of hydrogen bromide with unsaturated compounds was detected by the ESR method (in the photolysis of hydrogen bromide–cyclohexene mixtures). The resulting ESR spectrum was similar to that quoted by Abell and Piette[32].

Exact determination of the quantum yield at low temperatures in mixtures of hydrogen bromide and olefins is difficult, because the mixtures are polycrystalline and scatter light to a marked degree. In measurements involving ferric oxalate intensitometry only the number of quanta incident on an amount of mixture which virtually did not transmit light was estimated. The lower limit of the quantum yield obtained in this way for the hydrobromination of ethylene proved to be 150.

The chain length was also estimated on the basis of chromatographic data. In the gas-chromatographic analysis of the products of the low-temperature photochemical hydrobromination of ethylene[29] a considerable amount of 1,2-dibromoethane was detected in addition to ethyl bromide, the ethyl bromide : 1,2-dibromoethane ratio being 500 : 1. The presence of 1,2-dibromoethane in the reaction products shows that the reaction has a radical mechanism. If it is supposed that at low temperatures the reaction proceeds by the same mechanism as in the gas phase, 1,2-dibromoethane may form as a result of the recombination of radicals which propagate the chain hydrobromination of ethylene according to the following mechanism:

$$HBr + h\nu \rightarrow H + Br,$$
$$Br + C_2H_4 \rightarrow C_2H_4Br,$$
$$C_2H_4Br + HBr \rightarrow C_2H_5Br + Br,$$
$$C_2H_4Br + Br \rightarrow C_2H_4Br_2.$$

The chain length can be defined[16] as the number of molecules of the main product formed as a result of chain reaction per active centre. On the basis of the above mechanism, the chain length can be estimated as 250 units from the ethyl bromide : 1,2-dibromoethane ratio obtained.

Since in the determination of the quantum yield the amount of reaction products was found after heating the mixture, it is important to emphasise that the hydrobromination reactions occur in the solid phase below the melting points of the starting components. This is clearly shown in Fig. 6 in which we have plotted thermographic curves for the hydrogen bromide–ethylene system obtained when mixtures subjected to preliminary irradiation with various doses of ultraviolet light at 77°K were heated. The occurrence of reaction in the solid phase is also indicated by the considerable increase in the yield of ethyl bromide with time in an irradiated mixture. For example,

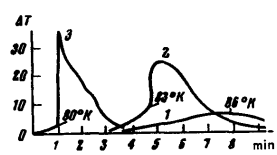


Fig. 6. Thermographic curves for equimolar mixtures of hydrogen bromide and ethylene; temperature of preliminary light irradiation 77°K:
1) Light irradiation dose $D = 0.6$ (arbitrary units), extent of reaction 15%; 2) $D = 0.9$, extent of reaction 14%; 3) $D = 39.5$, extent of reaction 37%.

the extent of reaction increases by 25–30% if the mixture is kept in the dark for 1 h at 77°K before measurements. At high light intensities the reaction is explosive and may occur when actually exposed to the light beam at 77°K. The shape of the thermographic curve is then similar to that of curve *3* in Fig. 6.

An interesting feature of the hydrobromination of ethylene at 77°K is that the rapid reaction is preceded by an induction period, the explosion itself always occurring after exposure to the same radiation dose[28]. This finding is clearly shown by the data presented in Table 4. Thus the induction period τ is inversely proportional to the intensity I, while the dose $D = I\tau$ = const., i.e. the development of the explosive chain reaction at low temperatures requires the accumulation of a specified concentration of active centres, which is clearly determined by the dose and not the intensity.

Another interesting feature of the photochemical hydrobromination is its marked dependence on the conditions of heat exchange with the surrounding medium. If, for example, the heat exchange is reduced, the rapid reaction begins after smaller radiation doses, and conversely if the heat exchange is increased, there is no reaction at all at the temperature of liquid nitrogen for low radiation doses. Here reaction occurs at higher temperatures. The above features of the photochemical hydrobromination of ethylene are associated with the possibility of stabilisation of active centres and show that in low-temperature chain reactions the properties of chain and thermal explosions are closely interlinked.

At low temperatures the frozen mixtures of hydrogen bromide with olefins are polycrystalline and it was of considerable interest to elucidate which features of photochemical chain hydrobromination are characteristic of the crystalline state and which are characteristic of the vitreous state. Transparent glasses are formed when allyl chloride and its liquid mixtures with hydrogen bromide are rapidly cooled to 77°K. When such glasses are exposed to ultraviolet irradiation at 77°K and then warmed, chain hydrobromination occurs in the solid phase below the melting point of the mixture. The quantum yield of the

TABLE 4. Dependence of the induction period τ in the hydrobromination of ethylene on the intensity of illumination (I) at 77°K*.

I/I_0	τ, s	ΔT, °K	ΔT_M, °K	η, %	D_{exp}
1	4.4	0.9	31	17.1	4.4
0.62	6.5	1.1	30	16.4	4.0
0.51	9.0	1.0	31	16.3	4.6
0.34	11.5	1.0	30	16.0	3.9
0.25	16.3	1.3	31	16.2	4.1
0.10	45.7	1.1	30	15.2	4.6
0.04	no explosion, on subsequent heating reaction occurs at higher temperatures				

* All the values in the table are averages from several experiments: ΔT is the temperature rise at the end of the induction period, ΔT_M the maximum temperature rise, η the extent of reaction, and $D_{expl} = I\tau$ the radiation dose resulting in explosion. The radiation dose is expressed in arbitrary units. The amount of radiation received by the specimen at maximum intensity I_0 from a PRK-7 lamp in 1 s was adopted as one unit.

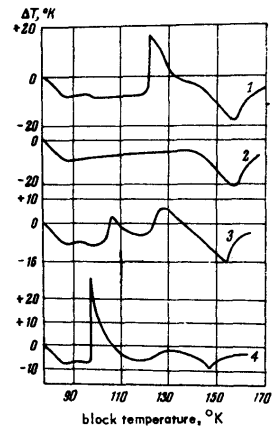


Fig. 7. Temperature variation of the difference between the specimen and block temperatures ΔT (deg) for allyl chloride and its mixtures with hydrogen bromide: 1) vitreous allyl chloride specimen; 2) crystalline specimen; 3) vitreous specimen irradiated with ultraviolet light at 77°K for 5 s; 4) similar specimen irradiated for 180 s.

low-temperature photochemical hydrobromination of allyl chloride is about 50. The occurrence of the reaction in the solid phase was confirmed with the aid of infrared spectra obtained in a special cuvette where the low-temperature photolysis could be carried out and the infrared spectra recorded.

Fig. 7 presents the results of a study of the hydrogen bromide–allyl chloride system by differential thermal analysis[30]. It is evident that the allyl chloride frozen to a glass crystallises at 110°K and melts at 136°K. The equimolar mixture of hydrogen bromide and allyl chloride behaves similarly.

When vitreous hydrogen bromide–allyl chloride specimens irradiated at 77°K are warmed, the thermograms (Fig. 7) reveal the occurrence of a new exothermic process at about 88°K. This process is associated with the hydrobromination since the temperature rise at 88°K is directly proportional to the amount of 3-bromo-1-chloropropane. The formation of 3-bromo-1-chloropropane as the main reaction product was confirmed by gas-chromatographic analysis. The effect of the duration of illumination on the form of the thermographic curves for the vitreous equimolar hydrogen bromide–allyl chloride mixtures is shown in Table 5.

The data in Table 5 show that the temperature of the start of reaction is independent of the duration of the preliminary illumination of the mixture at 77°K. This fact constitutes the most interesting peculiarity of the photochemical chain hydrobromination in the vitreous systems. In crystalline mixtures of allyl chloride and hydrogen bromide the temperature range in which the reaction takes place (the reaction occurs only on heating) depends on the duration of the preliminary irradiation of the mixture at 77°K. In its main outline the reaction is of the same type as in frozen mixtures of ethylene and hydrogen bromide.

The surprising finding that the temperature of the onset of reaction is independent of the duration of the preliminary

TABLE 5. Results of a thermographic study of the hydrogen bromide–allyl chloride system as a function of the time of the preliminary irradiation at 77°K*.

t	T_1	ΔT_1	T_2	ΔT_2	T_f	ΔT_f	t	T_1	ΔT_1	T_2	ΔT_2	T_f	ΔT_f
1	88	11	110	7.0	128	7.0	45	85.5	33.5	108	5.5	126	3
5	86.5	25.5	110	3.5	125	4.5	80	87.5	36		0.2	129	2
15	88	28.5	112.5	2.0	126	3	120	88	36	115	2	127	2
							240	89.5	39				

* t is the duration of irradiation (minutes) of the specimens at 77°K, T_1, T_2, and T_f are the temperatures of hydrobromination, crystallisation, and fusion respectively, ΔT_1 and ΔT_2 are the maximum temperature rises during the reaction and during crystallisation, and ΔT_f is the height of the fusion peak (°K).

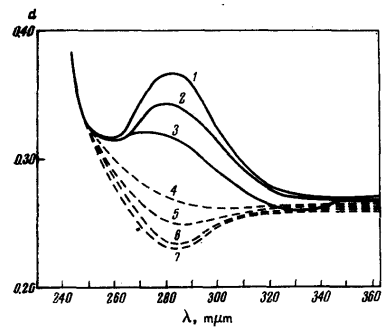


Fig. 8. Ultraviolet absorption spectra at 73°K: 1) non-irradiated mixture of hydrogen bromide and allyl chloride; 2) after irradiation with filtered light (313 mμm) for 25 min 41 s; 3) ditto after irradiation for 49 min 30 s; 4) mixture of hydrogen bromide and allyl chloride after heating to 103°K, spectrum recorded at 73°K; 5) mixture without complex after irradiation for 60 min with filtered light (313 mμm); 6) duration of irradiation 120 min; 7) duration of irradiation 180 min.

irradiation can be explained by supposing that 86–88°K constitutes the low-temperature limit of the softening of the hydrogen bromide–allyl chloride glass. In the glass-softening range there is a change[31] in properties of the system such as heat capacity, viscosity, specific volume, thermal conductivity, etc. In the given case the decrease in the viscosity of the system probably plays the main part, increasing the mobility of the reacting species and facilitating the initiation of the reaction by the active reaction centres stabilised at 77°K and produced during the preliminary irradiation. The rapid increase of the viscosity in the softening range is actually responsible for the virtually complete independence of the temperature of the onset of reaction of the dose of preliminary irradiation. The "healing" of the cracks formed in the glass at 77°K is a qualitative indication that the softening of the hydrogen bromide–allyl chloride glass occurs at temperatures below 90°K. The glass softening range was also determined thermographically from the jump in heat capacity. The thermograms of allyl chloride and of non-irradiated hydrogen bromide–allyl chloride mixtures reveal a weak endothermic process which begins at about 87°K.

The hydrobromination of olefins and halogeno-olefins occurs in systems where there is a possibility of donor–acceptor interaction which leads to the formation at low temperatures of unstable molecular compounds[33]. The role of such complexes in the formation of radicals under the action of light at low temperatures has already been mentioned in the first part of this review. Certain aspects of the participation of such complexes in low-temperature chain reactions are examined below, using the hydrogen bromide–allyl chloride system as an example[34].

Fig. 8 shows ultraviolet spectra of the hydrogen bromide–allyl chloride system. Spectrophotometric study of hydrogen bromide–allyl chloride films frozen on to a quartz plate at 80°K revealed an absorption band with a maximum at 283 mμm. When such mixtures are heated to 103°K and then cooled again to 80°K, this band vanishes irreversibly. The result shows that during condensation on to the cooled quartz plate hydrogen bromide and allyl chloride form a compound which is stable only at the temperature of liquid nitrogen.

Hydrogen bromide is an electron acceptor whereas allyl chloride can behave as an electron donor. In hydrogen bromide–propane mixtures, which were investigated at the same time, the 283 mμm band was not observed. The experimental data obtained suggest, when considered together, that the 283 mμm band of the hydrogen bromide–allyl chloride mixtures is probably due to a charge-transfer complex which forms during the condensation of the starting materials.

In a study of the effect of the amount of hydrogen bromide and allyl chloride on the intensity of the 283 mμm absorption band it was found that an increase in the concentration of either the donor or the acceptor causes a decrease in the intensity of the absorption band. The total amount of mixture was kept constant in these experiments. This type of variation of the intensity of the absorption band with mixture composition indicates that a 1 : 1 complex forms.

In order to elucidate the role of complexes in low-temperature reactions, a comparative study was made of the dependence of the extent of reaction on the duration of irradiation with filtered light (filter with a transmission maximum in the region of 313 mμm) of hydrogen bromide–allyl chloride mixtures with the absorption at 283 mμm characteristic of the complex, and mixtures in which there was no appreciable absorption in this region, the hydrogen bromide–allyl chloride system being heated to 103°K before irradiation with ultraviolet light at 77°K. As stated above, such heating breaks down the complex. Figs. 9 and 10 show the variation of the optical density at 283 mμm and of the extent of reaction with the duration of irradiation. The results obtained indicate the participation of unstable molecular compounds of hydrogen bromide and allyl chloride in the hydrobromination reaction. Data derived from thermographic analysis and infrared spectra show that the decrease of the optical density during irradiation is not associated with an appreciable occurrence of hydrobromination at 80°K. On the other hand, on raising the temperature (Fig. 10) the extent of reaction reaches almost 100%, and a high quantum yield indicates that a chain reaction takes place. Thus the data taken together suggest that at temperatures 77–80°K active centres are formed, probably mainly as a result of the photolysis of unstable molecular complexes.

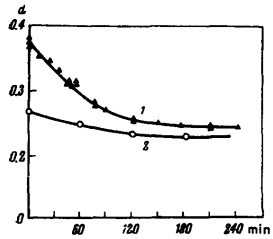


Fig. 9. Variation of optical density with the duration of irradiation in the system hydrogen bromide–allyl chloride at 73°K:
1) irradiation of mixture with complex;
2) irradiation of mixture without complex;
3) curve obtained by graphical subtraction of curve 2 from curve 1.

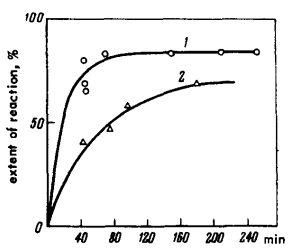


Fig. 10. Variation of the degree of reaction with the time of irradiation in the photochemical hydrobromination of allyl chloride:
1) reaction in the system with complex;
2) reaction in the system without complex.

At 77°K the active centres which initiate the hydrobromination of olefins can also form as a result of the reaction $HBr + h\nu \rightarrow H + Br$. The results obtained in a photometric study of the hydrogen bromide–allyl chloride system make it possible to estimate the contributions of various reactions to the formation of active centres. On the basis of these data, the formation of active centres under the action of light in the solid phase at 80°K can be represented thus:

$$\pi\overset{n}{\nearrow}\!\!\searrow C_3H_5Cl + HBr \rightarrow H + Br\,',$$

where π is the complex and n the number of active centres formed from the complex.

The curves in Figs. 9 and 10 permit an approximate estimate of the relative contributions of various modes of reaction. Comparison of the yields in the initial stage of the photolysis (Fig. 10, curve *1*) and after 1.5 h when all the complex has been almost completely used up indicates the greater effectiveness of the reaction occurring with participation of the complex compared with the reaction in the system without the complex. For example, during the period of existence of the complex $\tau = 0.2t$, where t is the time of irradiation of the mixture corresponding to 85% conversion, the reaction proceeds to the extent of 62%.

On the basis of the above mechanism and using the initial condition $\pi = \pi_0(HBr) = (HBr)_0$, a system of differential equations was set up, and solved with the aid of MN-7 non-linear modelling apparatus. Analysis of the curves obtained showed that, in the initial reaction stage, the formation of active species with the participation of the complex is several times faster than the formation of active species from hydrogen bromide, although the concentration of the complex is smaller than that of hydrogen bromide approximately by a factor of ten. Thus, in contrast to gas and liquid phases, where chain initiation occurs as a result of the photolysis of hydrogen bromide, in the solid phase at low temperatures the active centres are formed mainly under the action of light from unstable intermediate compounds of the donor–acceptor type.

The development of a chain reaction in the solid phase is also affected by particular features of the chain termination reactions. Study of the dependence of the degree of hydrobromination of ethylene η on the light irradiation dose in liquid (112°K) and solid (77°K) phases showed that the degree of reaction in the solid phase is smaller for the same light irradiation dose[30]. In the liquid phase η increases linearly with dose, while in the solid phase it decreases as the dose is increased, which is probably an indication of a decrease in chain length with increase in the concentration of stabilised active centres. Chain termination in the solid phase probably occurs as a result of recombination of the active centres responsible for chain propagation with stabilised active reaction centres.

The possibility of accumulation at low temperatures of considerable concentrations of active centres exerts a significant influence also on the chain propagation reactions. In frozen hydrogen bromide–ethylene mixtures the accumulation of stabilised active centres is accompanied by a slow reaction whose rate depends on the concentration of the centres. Under certain conditions, when the rate of heat generation by the reaction exceeds the rate of heat removal from the system, a vigorous exothermic process takes place by a thermal explosion mechanism.

Semenov regarded the rapid photochemical hydrobromination of ethylene at 77°K as an unusual kind of chain explosion, in which the increase in the number of stabilised active centres entering into reaction is due to the heat of the reaction itself.

The possible mechanism of the reaction can be represented as follows. Most of the active centres formed under the action of light at 77°K are stabilised, and only in rare cases, for example on recombination of two active centres near a third centre, can an individual reaction chain of several hundreds of units arise. The occurrence of such a reaction chain is accompanied by an intense thermal wave (the hydrobromination of olefins is an exothermic reaction), which causes new, stabilised active centres to enter into the reaction. Semenov called such a mechanism the development of a straight chain which undergoes branching occurring with the aid of elementary thermal waves. Thus the results obtained in the study of low-temperature photochemical hydrobromination of olefins, together with data on low-temperature polymerisation, enabled Semenov to formulate the hypothesis of the important role of energy chains in the occurrence of chemical reactions at low temperatures.

IV. RAPID SPONTANEOUS CHEMICAL REACTIONS AT LOW TEMPERATURES

In the first two sections low-temperature reactions initiated by light were examined. This section deals with

TABLE 6. Results of a thermographic study of certain chemical reactions at low temperatures*.

System	T_f, °K component I	T_f, °K component II	T(rapid reaction), °K	Principal products	Yield, %
Chlorine–ethylene	104	172	106,119,171	1,2-dichloroethane	97
Chlorine–propene	88	172	91,111,147	1,2-dichloropropane	92
Chlorine–isobutene	133	172	112,130	1,2-dichloro-2-methylpropane	80
Chlorine–styrene	242	172			
Chlorine–thiophen	245	172			
Bromine–propene	88	266	117,158,193	1,2-dibromopropane	98
Bromine–isobutene	133	266	120,133,188	1,2-dibromo-2-methylpropane	96
HBr–isobutene	133	186	84,119,150	2-bromo-2-methylpropane	98
HCl–isobutene	133	159	100,119,133,155	2-chloro-2-methylpropane	93
N_2O_4–propene	88	262	238	nitro-nitrate and nitroso-nitrate	
N_2O_4–isobutene	133	262	200	ditto	
N_2O_4–but-1-ene	143	262	233	»	
N_2O_4–hex-1-ene	133	262	241	»	
N_2O_4–cyclohexene	169	262	207	dinitrocyclohexane and nitro-nitrates	
N_2O_4–cyclopentadiene	188	262	183	ditto	
Nitric oxide–oxygen	109	54	88	nitrogen dioxide	100
Nitric oxide–chlorine	109	172	108,143,157	nitrosyl chloride	100
HBr–chlorine	186	172	91,168	hydrogen chloride and hydrogen bromide	100
HCl–nitrogen dioxide	159	262	193	nitrosyl chloride, chlorine, and water	97
Bromine–toluene		266	131,203	hydrogen bromide and substituted toluene	95

* The initial component ratios are 1 : 1, except for nitric oxide with oxygen and chlorine for which the ratios are 2 : 1. In the reaction temperature column the temperatures at which the main bulk of the substance reacts are underlined. Chlorine reacts with thiophen and styrene at the instant of condensation. The nitro-compounds were analysed spectroscopically.

certain peculiarities of the kinetics of a large number of various spontaneous rapid chemical reactions at very low temperatures, discovered in the Department of Chemical Kinetics. Table 6 presents part of the results obtained in a thermographic study of certain chemical reactions at low temperatures[35-38]. In order to eliminate the possibility of reaction in the gas phase at the instant of condensation, the starting materials were frozen in the reaction vessel in the form of individual layers. The technique of the thermographic investigation has been described[36,40].

It is evident from the data in Table 6 that the following reactions can take place at low temperatures: addition of halogens, hydrogen halides, and nitrogen tetroxide to double bonds; inorganic addition reactions ($NO-O_2$ and $NO-Cl_2$ systems); inorganic exchange substitution reactions ($HBr-Cl_2$ system); substitution in aromatic compounds (bromine–toluene system); inorganic redox reactions (NO_2–HCl system).

The technique involving the freezing of the initial components as individual layers prevents their coming into contact at elevated temperatures and makes it possible to verify the possibility of the spontaneous occurrence of the reactions at low temperatures. However, the mixing of the initial reactants is then so poor that the reactions must be hindered. It may be expected that in homogeneous mixtures the reactions would occur at much lower temperatures. To test this hypothesis, a study was made of certain reactions in condensates prepared by freezing out from molecular beams[41]. The molecular beam method for the study of chemical reactions at low temperatures was developed by Semenov and Shal'nikov[42]. Recently this method was successfully used to study low-temperature

TABLE 7. Low-temperature halogenation and hydrohalogenation of unsaturated compounds in mixtures prepared by the molecular beam method*.

System	T_f, °K component I	T_f, °K component II	T(rapid reaction), °K	Principal products	Yield, %
Bromine–ethylene	104	266	103	dibromoethane	93
Bromine–propene	88	266	90	1,2-dibromopropane	95
Chlorine–cyclohexene	169	172	98	dichlorocyclohexane	90
Bromine–cyclopentadiene	188	266	98		
HBr–cyclopentadiene	188	186	103		

* The reaction temperatures indicated are averages from a large number of experiments. The discrepancies are within the range of 5 deg.

polymerisation[43]. Condensation under molecular beam conditions yields a mixture which is closest to the molecular state; even the freezing of mixtures subjected to preliminary mixing in the gas phase can involve considerable separation into layers. Table 7 quotes as an example the results obtained in a study of certain halogenation and hydrohalogenation reactions of unsaturated compounds. The apparatus and technique have already been described[41].

Comparison of Tables 6 and 7 shows that in thoroughly blended mixtures the reactions can take place entirely at much lower temperatures. Bromination of ethylene and propene occurs at temperatures close to the melting points of the olefins. In the chlorine–cyclohexene system the reaction occurs in the solid phase at 98°K. This is the temperature of the glass–crystal phase transition. When these substances are frozen into two separate layers, the chlorination occurs at 169°K, i.e. near the melting points of the initial components. It is interesting that, due to their high reactivity, propene and bromine cannot be condensed on a surface cooled with liquid nitrogen at deposition velocities of 10^{17} mol. s^{-1}. This can only be done by reducing the rate of deposition by a power of ten.

Examination of Tables 6 and 7 reveals certain interesting peculiarities of chemical reactions at low temperatures.

1. Many chemical reactions of various types can occur spontaneously (in the absence of special initiation) in the condensed phase even at temperatures as low as the boiling point of liquid nitrogen.

2. These reactions often have high explosive velocities, which means that it is usually necessary to work with amounts of the order of 10^{-3}–10^{-4} mole.

3. A characteristic feature of low-temperature reactions involving addition of halogens to olefins is that they are quantitative and specific. As a rule only one substance (addition product) is obtained in a yield close to 100%. This may be compared with reactions in gas and even in liquid phases at elevated temperatures[16] in which a large amount of substitution products is usually obtained.

4. Low-temperature reactions are highly selective. For example, it has been shown that chlorine adds readily to ethylene but not to acetylene. Nitrogen tetroxide adds readily to propene but not to ethylene. Hydrogen bromide adds to isobutene in the dark and to propene only under the action of ultraviolet light, etc.

5. At low temperatures each reaction usually has a definite characteristic (critical) temperature, as a rule associated with a phase transition (fusion, polymorphic

transformation, crystallisation). It is interesting that in the reaction of nitrogen tetroxide (N_2O_4) with olefins the reaction temperature depends on the conditions of heat exchange between the system and the surrounding medium[44]. Improvement of heat exchange displaces the onset of reaction towards higher temperatures and conversely, when heat exchange with the surrounding medium is poor, the reaction occurs at lower temperatures. This effect of heat exchange conditions on reaction rate is usually characteristic of reactions which proceed by a thermal explosion mechanism[16].

In an examination of the peculiarities of spontaneous low-temperature reactions it is necessary to consider the origin of reactions at low temperatures and their mechanism. The solution of these problems was facilitated by a comparative study of the addition reactions of halogens to olefins at low and normal temperatures. Let us consider as an example the bromination of cyclohexene in carbon tetrachloride solution[45]. Study of this reaction in the temperature range 263–313°K (Fig. 11) showed that it has a negative temperature coefficient and that the reaction rate follows the equation $W = k(Br_2)^2(C_6H_{10})$. These findings can be explained on the hypothesis that the reaction proceeds via a stage in which an intermediate molecular complex forms by the mechanism

$$(1)\ Br_2 + C_6H_{10} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [Br_2 \cdot C_6H_{10}];\quad (2)\ [Br_2 \cdot C_6H_{10}] + Br_2 \rightarrow \text{reaction product}, \qquad (I)$$

$$(1')\ 2Br_2 + C_6H_{10} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [C_6H_{10} \cdot 2Br_2];\quad (2')\ [C_6H_{10} \cdot 2Br_2] \overset{k_3}{\rightarrow} \text{reaction product}, \qquad (II)$$

where $[Br_2.C_6H_{10}]$ or $[C_6H_{10}.2Br_2]$ are unstable molecular compounds. Application of the steady-state method to both mechanisms results in the same expression for the rate of consumption of bromine:

$$(3)\ -\frac{d(Br_2)}{dt} = Kk_3(Br_2)^2(C_6H_{10}),$$

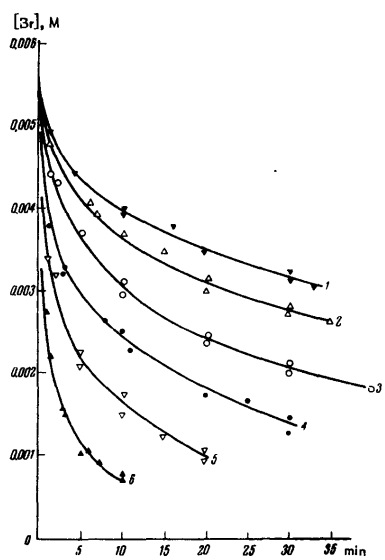


Fig. 11. Kinetic curves for the bromination of cyclohexane in carbon tetrachloride at different temperatures (°K):
1) 313; 2) 303; 3) 293; 4) 283; 5) 273; 6) 263.

where $K = k_1/k_2$ is the equilibrium constant for reactions (1) and (1'). This expression was obtained on the assumption that $K \ll 1$, and is consistent with the experimental order of reaction. Eqn. (3) shows that the experimental rate constant results from a combination of several constants:

$$k_{exp} = \frac{k_1k_3}{k_2} = \frac{k_1^0e^{-\frac{E_1}{RT}}k_3^0e^{-\frac{E_3}{RT}}}{k_2^0e^{-\frac{E_2}{RT}}} = k_0e^{-\frac{E_1-E_2}{RT}}e^{-\frac{E_3}{RT}} = k_0e^{\frac{\Delta H+E_3}{RT}},$$

where $\Delta H = E_1 - E_2$ is the heat of the complex-formation reaction. It may be assumed that over a small temperature range

$$\frac{\partial \ln k_{exp}}{\partial T} = \frac{\Delta H + E_3}{RT^2}.$$

The formation of molecular complexes occurs with evolution of heat ($\Delta H < 0$) and, when $E_3 < |\Delta H|$ and $E_3 + \Delta H < 0$, the rate of reaction falls with increase in temperature, i.e. there is a negative temperature coefficient.

The existence of a negative temperature coefficient is evidence that the reaction occurs in stages and shows that the heat of the rate-limiting stage, involving the formation of an intermediate, is higher than the activation energy for the conversion of the intermediate into the final reaction product. In a study of this reaction by differential thermal analysis (DTA) in a special vacuum reaction vessel it was shown that the reaction is nearly of first order. In the DTA method the observed temperature rise was mainly due to the heat of the rate-limiting stage. The result obtained is probably an indication that mechanism (II) is to be preferred for the bromination of cyclohexene.

The data on the kinetics of the bromination of cyclohexene in Fig. 11 show that the rate of reaction increases in accordance with the Arrhenius law as the temperature is reduced, but with, as it were, a negative activation energy $E = -12$ kcal mole^{-1}. This value is comparable to the heat of bromination of cyclohexene but exceeds the heat of formation of donor–acceptor complexes available in the literature, which are usually 1–5 kcal mole^{-1}.[13] This inconsistency suggests that in the halogenation reactions the intermediate molecular complex, whose structure is similar to that in the pre-reaction stage, is an aggregate (self-solvate) consisting of several bromine and cyclohexene molecules. As the temperature is reduced, the probability of the formation of such aggregates increases.

If the rate of halogenation of olefins is limited by the complex-formation stage, it follows in principle from the mechanism A + B $\rightleftharpoons$ (AB) $\rightarrow$ final product (A and B are the olefin and the halogen and AB is the intermediate complex) that conditions are possible in which the complex does not form and therefore the halogenation reaction cannot occur under the usual conditions. The bromination of tetrachloroethylene may be quoted as an example.

It has been demonstrated spectrophotometrically that at room temperature in the dark and in the absence of oxygen tetrachloroethylene does not react with bromine in carbon tetrachloride solution. When the mixture was kept at 253°K for 1.5 h, dibromotetrachloroethane was formed in 18% yield. This example clearly demonstrates the role of low temperature. In contrast to the usual postulates of classical chemical kinetics and our everyday experience, a reaction which does not take place in the liquid (condensed) phase begins to occur at a high rate when the temperature

is reduced. The occurrence of the bromination of tetrachloroethylene at low temperatures is evidence of the existence of highly active intermediate compounds responsible for the reaction and stable only at low temperatures. In the present author's view, such compounds are complexes of the donor–acceptor type.

On the other hand, it is also evident from the mechanism $A + B \rightleftharpoons (AB) \rightarrow$ final product that conditions may be found in which the relative rates of the individual reactions are such that the main effect is accumulation of the complex. When this is so, the use of low temperatures makes it possible to separate the complex-formation stage from the stage involving the conversion of the complex into final products. As an example, the results of a study of the bromine–propene system may be quoted[39].

Fig. 12 presents the results of the thermographic analysis of the bromine–propene mixture, with the components frozen into separate layers. The rapid reaction was preceded by two exothermic processes, one of which followed immediately after fusion of propene and occurred in the range between -185° and -156°C. It was shown that the evolution of heat in this temperature range is due to the dissolution of solid bromine in liquid propene and the formation of bromine–propene complexes, the heat of formation being about 5 kcal mole^{-1}. The second exothermic process occurred in the range between -156° and -125°C and preceded the reaction. This process may be associated with the segregation of the complexes into a separate phase and their association.

The use of low temperatures not only permits the separation of the stages involving the formation of the complex and the final product but also allows the accumulation of the intermediate complexes. For example, this can be done by repeated heating and cooling of the bromine–propene system in the temperature range between -196° and -156°C. The accumulation of complexes in this process is indicated by the fact that the amount of propene which may be evacuated from the bromine–propene system, for example at -145°C, decreases with the number of the above operations. The thermograms in Fig. 12 show that preliminary accumulation of complexes to a sufficiently high concentration results in the occurrence of rapid explosive reactions at -125°C. A relation between the complex-formation reaction and the bromination of propene is suggested by the fact that the magnitude of the exothermic peak at -125°C, corresponding to the reaction, depends on the number of heating and cooling cycles of the mixture in the temperature range between -196° and -156°C.

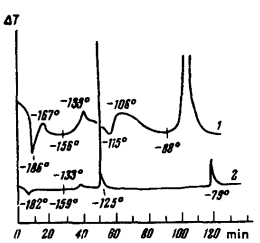


Fig. 12. Thermographic curves for bromine–propene mixtures:
1) specimens frozen in separate layers;
2) after preliminary mixing and accumulation of complex (temperatures in °C).

Additional proof of the participation of unstable molecular compounds in low-temperature halogenation of olefins was obtained with the aid of electronic absorption spectra, using bromination of propene as an example. In contrast to thermography, the spectroscopic method makes it possible to follow in greater detail the changes occurring in the initial molecules and in many cases helps elucidate the nature of the complexes formed[46].

The ultraviolet spectra of solid condensed films of bromine, propene, propane, and 1,2-dibromopropane were obtained with an SP-700 recording spectrophotometer. The test substances and their mixtures in various proportions were frozen in a vacuum cuvette on a quartz plate cooled with liquid nitrogen under conditions approximating to those in a molecular beam. The temperature of the film was measured with a thermocouple. At low temperatures propane is almost transparent up to 200 mμm. In the spectrum of solid propene there is a weak band in the region of 217–250 mμm. In the spectrum of solid bromine in amounts of 10^{-6} mole there is a band with an absorption maximum in the region of 280 mμm. When bromine is highly diluted with propane (1.8×10^{-7} mole of bromine and 4×10^{-4} mole of propane), the absorption in this region falls to an optical density of 0.01.

In the study of the bromine–propene system the initial components were frozen on to a cooled quartz plate in several successive layers. To ensure a more uniform distribution, bromine was diluted with propane in a number of experiments. The spectra of the bromine–propene system are presented in Fig. 13, which shows that in the spectrum of the mixture where the bromine was diluted with

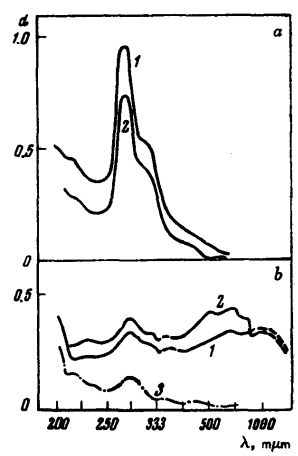


Fig. 13. Ultraviolet absorption spectra of the bromine (6×10^{-8} mole)–propene (9×10^{-4} mole) system:
a) spectra in the presence of added propane: 1) at 80°K; 2) mixture kept at 80°K for 1.5 h and then heated twice to 100°K [above m.p. of propene (83°K)], spectrum recorded at 73°K;
b) spectra of bromine–propene mixture (without propane): 1) at 80°K; 2) after 1.5 h at 80°K; 3) after heating to 100°K and recooling to 80°K, spectrum recorded at 80°K. The wavelength scale on the SP-700 spectrophotometer is expressed in cm^{-1}. In the Soviet chemical literature it is usual to express the wavelengths in the visible and ultraviolet spectra in millimicrons. The recalculation results in a non-linear scale.

propane there is an intense band in the region of 274 mμm. On the long-wavelength side of the band there is a distinct inflection in the region of 312.5 mμm. The absorption at the point of inflection is smaller at least by a factor of two than in the maximum of the band. When the temperature is raised, the band widens somewhat and its intensity falls irreversibly.

The spectrum of bromine–propene mixtures differs radically from that of the bromine–propane system. The much higher absorption intensity in the mixtures with propene indicates a pronounced donor–acceptor interaction between the bromine and propene. It may be supposed that in the bromine–propene system the bands in the region 274–312 mμm are due to 1:1 and 1:2 molecular charge-transfer complexes. The energy of an optical transition from the ground to an excited state in such donor–acceptor complexes is described by the approximate equation

$$h\nu = I - E - \frac{e^2}{r},$$

where I is the ionisation potential of the donor, E the electron affinity of the acceptor, and e^2/r the energy of the interaction of the components of the system, bearing opposite charges, at a distance r.[13,19] In binary complexes of bromine with various acceptors r varies in the range 3.6–4.5 Å, depending on the mutual disposition of the donor and acceptor molecules[22]. Adopting the average value of 4 Å for r and 1.2 eV for the electron affinity of bromine[22], the ionisation potential of propene was estimated as 9.3 eV from Eqn. (1) for the charge-transfer spectrum at $h\nu$ = 278 mμm. The satisfactory correlation of this value with $I_{C_3H_6}$ = 9.65 eV found for propene in the gas phase confirms the validity of the hypothesis that in the bromine–propene mixture molecular charge-transfer complexes are responsible for the absorption in the region 280–310 mμm. In the condensed phase the ionisation potential of the molecule should be lower than in the gas phase. This may be due to a certain energy gain resulting from the polarisation of the surrounding molecules by the positively charged ion and the free electron.

In the bromine–propene system undiluted by propane there are a number of new bands in addition to those at 278–312 mμm. The greatest interest attaches to a broad band in the region of 500–1000 mμm (Fig. 13, curve *1*). The intensity of this band is higher than that in the region of 278 mμm.

It is interesting that, on keeping the mixture at temperatures close to 77°K for a specified time, the intensity of the band in the region of 500–1000 mμm increases. On the other hand, if the mixture temperature is raised to 100°K (m.p. of propene is 88°K), the absorption in the range 500–1000 mμm vanishes irreversibly (Fig. 13*a*, curve *3*). The band in the region of 278 mμm persists to some extent. These results show that intermediate compounds which absorb between 500 and 1000 mμm are mainly responsible for the low-temperature bromination of propene.

The presence of the broad band between 500 and 1000 mμm in the spectrum of the bromine–propene mixture at low temperatures is evidence, in the author's view, that not binary complexes but strongly linked reactive aggregates of the type DADADADA, where D is the donor and A the acceptor, are responsible for the absorption. The existence of similar stable compounds with a chain structure at low temperatures has been described in the literature[47]. On energy grounds, at low temperatures such aggregates are more likely than binary compounds.

In associated compounds absorbing between 500 and 1000 mμm the molecular and intermolecular distances are markedly altered, with loosening of the double bond and its pronounced polarisation. Preliminary data from infrared spectra apparently confirm this conclusion because bands at lower frequencies have been detected in the spectra of frozen solid mixtures of bromine and propene in the region of double bond stretching vibrations (1632 cm^{-1}).

The formation of highly polarised associated molecular compounds of the donor–acceptor type in bromine–propene mixtures at low temperatures can probably facilitate electron transfer and the spontaneous appearance of ionised states. It is seen from the data in Fig. 13*b* that the energy of the non-equilibrium absorption of a light quantum (electron-transfer spectrum) at the long-wavelength edge of the absorption band of the aggregates at 2 μm is already as much as 0.5 eV. The energy of thermal excitation may be smaller than this and therefore it is reasonable to suppose that at low temperatures in strongly interacting complexes, formed during condensation with considerable evolution of heat, ions or radical-ions, facilitating the subsequent reaction, may form spontaneously.

The formation of molecular complexes with charge transfer probably plays a definite role also in liquid-phase halogenation of olefins at room temperature. This is indicated by the negative temperature coefficient characteristic of these reactions and the correlation between the rates of halogenation of olefins and their ionisation potentials I observed by the present author. As a rule, the lower the ionisation potential of the olefin, the higher is the rate of halogenation. For example the rates of bromination of various olefins increase in the series

ethylene	< propene	< but-1-ene	< isobutene	< trimethylethylene	< tetramethylethylene.
10.51	9.65	9.61	9.35	8.80	8.30 eV

A similar variation occurs also for olefin chlorination reactions. It was to be expected because a decrease of ionisation potential is accompanied by an increase in the concentration of complexes, in the degree of electron transfer, in dipole moment, etc. and ultimately the appearance of ionised states is facilitated. Definite correlations between olefin ionisation potentials, their polarity, and reaction temperatures obtain also in the low-temperature nitration of unsaturated compounds with nitrogen tetroxide.

It may be assumed that under the same conditions of heat exchange with the surrounding medium the reactivity of the olefin is higher the lower is the temperature of the onset of explosive reaction. The data in Table 6 suggest the following reactivity series for olefins in low-temperature nitration with nitrogen tetroxide

	isobutene	< but-1-ene	< propene,	hex-1-ene
Ionisation potential	9.35	9.61	9.65	9.59
Dipole moment	0.49	0.37	0.35	0.34

The higher is the polarity of the olefin, the lower is the temperature at which it can be nitrated. However, examination of more extensive experimental data shows

that the reactivity of olefins in relation to halogens and nitrogen tetroxide is not entirely determined by the dipole moment,

In the investigation of spontaneous low-temperature reactions it is important to obtain direct experimental proof of the formation of active centres when simple valence-saturated molecules interact in the absence of light. The author was able to demonstrate by the ESR method the formation of radicals in the interaction between tetranitromethane and cyclohexene, tetramethylethylene, and certain other olefins. The experiments were made in the dark at room temperature. Fig. 14 presents as an example the ESR spectrum obtained for mixtures of tetranitromethane with C_6H_{10}. It was shown spectrophotometrically that tetranitromethane can form charge-transfer complexes with olefins. The fact that an ESR signal can be obtained from such mixtures in the absence of light is an indication that, even in the absence of light, there is a complete electron transfer in the system, resulting in the formation of paramagnetic radical states. The ESR spectrum in Fig. 14 has a hyperfine structure consisting of five lines which probably indicates the interaction of the unpaired electron with the nuclei of two nitrogen atoms.

In conclusion it must be emphasised that the sum total of the experimental data, obtained mainly for halogenation and nitration of olefins, permits an examination of the mechanism of fast spontaneous low-temperature chemical reactions in the most general form. The first stage of the addition reaction occurs during the condensation of the starting materials and results mainly in the formation of molecular 1:1 or 1:2 compounds. In the halogenation of olefins the formation of such complexes constitutes only the initial stage of the reaction and cannot as a rule lead to the spontaneous occurrence of the reaction at low temperatures. The results of the spectroscopic study of the bromine–propene system show that at low temperatures not only molecular 1:1 or 1:2 compounds but also highly polar aggregates can form. The existence of such aggregates, which probably have a chain structure, is thermodynamically more favourable at low temperatures. Their formation should be accompanied by the evolution of considerable amounts of heat and may lead to the spontaneous appearance of active centres which initiate the addition reaction. The formation of final products usually occurs at higher temperatures at the instant of a phase transition. For this reaction to occur, it is probably necessary that a small activation barrier, associated with the elastic forces of the lattice, be overcome. The most favourable conditions for this occur in a phase transition, where molecules require a certain mobility. The presence of the previously formed chain structure at the instant of the phase transition retards molecular rotation and preserves their orientation which is favourable for the addition reaction. As a result, only one product is formed in quantitative yield. When the olefins and the halogen are frozen in separate layers, the stages involving the formation of the complexes and the final products may be separated. When the components are thoroughly mixed, for example on condensation under molecular beam conditions, all the stages merge and the halogenation reactions occur at temperatures close to that of liquid nitrogen. The occurrence of the reaction via a series of successive stages influences the activation energy for the overall process. The formation of unstable and probably strongly solvated exothermic molecular compounds decreases the effective activation energy by their heat of formation. When aggregates are formed, this effect is very considerable and may greatly facilitate low-temperature reactions.

Fig. 14. ESR spectrum of a mixture of tetranitromethane and cyclohexane at 293°K.

The results obtained suggest also a somewhat different mechanism for reactions in which there is donor–acceptor interaction at low temperatures. Apparently the role of molecular compounds and their aggregates does not consist solely in the facilitation of the initiation of the active centres, and their formation in all probability results in the conversion of the two-component system into a system of oriented molecules in which extensive electron transfer takes place and all the conditions required for reactions which proceed by the collective interaction mechanism, proposed earlier by Semenov to explain rapid low-temperature polymerisation reactions without activation energy[48], are thereby provided. In a polarised aggregate conditions are set up during the electron transfer process, as a result of the presence of markedly loosened and readily broken bonds, in which there is simultaneous dissociation of the double bonds and the bonds in the halogen molecules, new carbon–halogen bonds being formed. If the redistribution of electron density between the halogen and olefin molecules is insufficient for spontaneous propagation of the reaction by the above mechanism, then conversion of the chain, formed as a result of the intermolecular interaction, into the final product is possible by way of energy chains. The reactions examined are exothermic and are accompanied by the evolution of a considerable amount of heat. The energy evolved in the formation of the aggregate of the initial molecules can readily migrate at low temperatures along the chain of strongly interacting and favourably oriented molecules. As a result, neighbouring molecular complexes may be excited, and the entire chain may be converted into the final product virtually without activation energy.

Thus study of chemical reactions at low temperatures permits a closer approach to the solution of the principal problem in chemistry — the elucidation of the fundamental mechanism of the interaction of two species, and opens a route to fundamentally new chemical syntheses.

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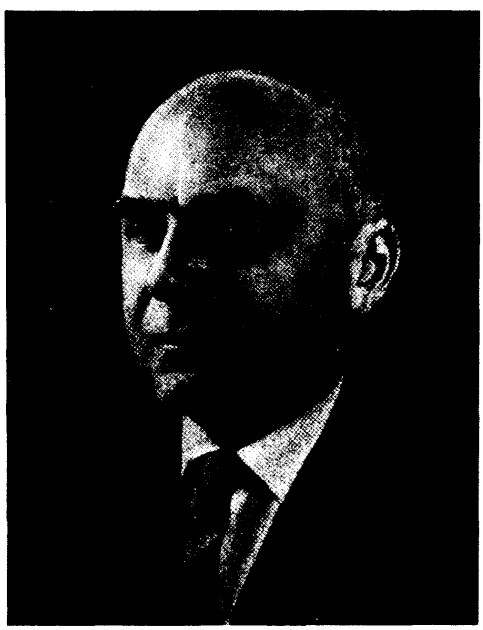

ALEKSANDR NIKOLAEVICH TERENIN

Deeply respected Aleksandr Nikolaevich!

The Editorial Board of the journal "Uspekhi Khimii" congratulates you heartily on your seventieth birthday. Your outstanding investigations in the field of physical chemistry have entered into the gold reserves of chemical science. The Editorial Board of "Uspekhi Khimii" is grateful to you for constant active assistance, and wishes you, dear Aleksandr Nikolaevich, good health and many years of life and creative work.

Editorial Board of "Uspekhi Khimii"

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THE CHEMISTRY OF THE BERYLLIDES

G. V. Samsonov

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INTRODUCTION

Compounds of beryllium with other metals are of great scientific and practical interest, since many of them have high melting points, relatively low specific gravity, high hardness, and also specific nuclear characteristics, which are united in a series of beryllides with specified properties.

Several equilibrium diagrams of beryllium–metal systems have now been investigated, the crystal structures of many beryllide phases have been studied, some of their physical, chemical, and technological properties have been studied, and definite ideas are beginning to accumulate about their crystal chemistry, electronic structure, and chemical bonding, which makes it possible to sum up all these investigations and to survey the information about compounds of beryllium with metals which is scattered in the literature.

I. BERYLLIDES OF GROUP I METALS

A. BERYLLIDES OF THE ALKALI METALS

The reaction of beryllium with the alkali metals has been little investigated[1]. Beryllium is stable up to 600°† in molten lithium, sodium, and potassium, but starts to dissolve at higher temperatures, owing to oxidation by the oxygen present in these metals[2]. According to the data given in a review[1], with the alkali metals (other than lithium) the size factor is so unfavourable that the probability of alloys being formed with beryllium, and also the possibility of their being miscible in the liquid state, are very small. Nevertheless, there have been reports[1,3] of the existence of potassium beryllide Be_2K, having $MgCu_2$-type cubic structure and of its being apparently quite a stable compound. There is no information about alloys of beryllium with sodium, rubidium, or caesium[4–6].

B. BERYLLIDES OF THE METALS OF THE COPPER SUBGROUP

Beryllium–copper system. Alloys of beryllium and copper have been studied in detail in connection with their great practical value (the beryllium bronzes). The equilibrium diagram of the Be–Cu system, first described in detail by Hansen[7] in the region from 0 to 35% Be, was subsequently repeatedly investigated and refined[8–14], the results being surveyed in reviews[1,15,16]. Fig. 1 shows the diagram of this system after Vol[15]. There are three beryllide phases: CuBe in the region of the β phase, $CuBe_2$, and $CuBe_3$ in the region of the δ phase; the existence of the phase Cu_2Be reported by Oesterheld[17] has not been confirmed by subsequent investigations[1].

The diagram shown in Fig. 1 has been confirmed completely by studies of diffusion in the Be–Cu system[18]. It was shown that the greatest diffusion coefficients and the least activation energy correspond to phases γ and δ, that is, to the approximate region of the compound CuBe.

† Temperatures are in °C throughout this article, except when °K is specifically mentioned (Ed. of Translation).

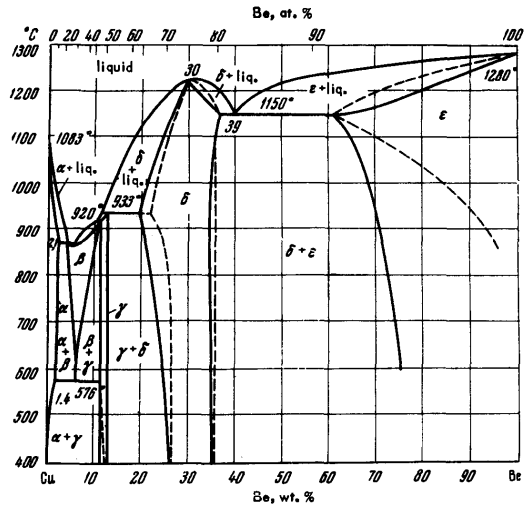

Fig. 1. Equilibrium diagram of the beryllium–copper system.

The physical and chemical properties of the copper beryllides (except for hardness) have hardly been studied (Table 1). The hardness of the quenched alloys whose compositions almost precisely correspond to beryllides[10], is relatively high and rises from CuBe to $CuBe_2$, then falls again slightly for $CuBe_3$. All the beryllides have a homogeneity region, the breadths of which have still not been found with sufficient accuracy. The properties (electrical resistivity, Hall constant, carrier current mobility) of copper–1.75 wt.% beryllium alloy, which is a mixture of the α and γ phases, have been studied in detail[19]. The resistivity of such alloys is ~7 $\mu\Omega$ cm.

It is difficult to prepare copper beryllides by melting the components together, owing to the great loss of beryllium at high temperatures; the best results are secured by making use of previously prepared copper–beryllium hardeners. The simplest method of making the beryllides is by powder metallurgy: by sintering copper and beryllium powders; according to Raub and Plate[20] the reaction between the compressed powders has begun even at 678°.

The beryllium–silver system has been studied[17,21,22]; Winkler[22] obtained the most reliable results, from which the diagram in Fig. 2 is constructed. There are two beryllides in the system: $AgBe_2$[23] and $AgBe_{12}$[24]. Both these phases are cubic, but $AgBe_2$ has a rather wider homogeneity region. Powder metallurgy is the most convenient method for obtaining silver beryllides, especially hot pressing of mixtures of the powders.

Beryllium–gold alloys were investigated by Winkler[22] and Chatterjee[25,26]; Fig. 3 shows the equilibrium diagram of the Au–Be system according to Winkler[22] and Fig. 4 the accurate phase diagram‡ of this system[26]. The following beryllide phases have been found in the system and identified by X-ray diffraction[1,26]: Au_3Be (β), Au_2Be (γ), AuBe (δ), $AuBe_3$ (ϵ), and $AuBe_5$ (η), and also, with great probability, phase $AuBe_{12}$, which is stabilised on replacing some of the Au atoms by W atoms[24]. At the same time the existence of the beryllide Au_4Be_3, stated by

‡ α is a solid solution of Be in Au, θ a solid solution of Au in Be.

TABLE 1. Properties of the beryllides of metals of the copper subgroup.

Beryllide	Be, wt. %	Structure	Type	Lattice parameters, Å		c/a	Density, g cm^{-3}	M.p., °C	Vickers hardness, kgf mm^{-2}
				a	c				
CuBe	12.4	cub.	FeSi	2.703 [23]	—	—	5.0 [15]	~ 920 [15]	311 [10]
$CuBe_2$	22.2	cub.	$MgCu_2$	5.952 [23,27]	—	—	5.277	~1140 [15]	517 [10]
$CuBe_3$	29.9	cub.	—	5.887 [23,27]	—	—	4.6 [15]	~1220 [15]	435 [10]
$AgBe_2$	14.3	cub.	$MgCu_2$	6.300 [23]	—	—	6.69 [22]	~1180 [22]	—
$AgBe_{12}$	50.2	tetr.	—	7.284 [1]	4.246	0.583	3.19 [1]	—	—
Au_3Be	1.51	tetr.	—	—	—	—	—	595 [22]	—
Au_2Be	2.25	tetr.	—	6.136 [26]	5.222	0.9	—	~645 [22]	—
AuBe	4.38	cub.*	FeSi	4.668 [28]	—	—	13.55 [28]	~730 [22]	—
$AuBe_3$	12.1	cub.**	—	—	—	—	—	—	—
$AuBe_5$	18.7	cub.	$MgCu_2$***	6.097 [25,29]	—	—	7.10 [25,29]	~1150 [22]	—
$AuBe_{12}$	35.7	tetr.	—	7.243 [30]	4.252	0.587	4.55 [30]		

* According to Chatterjee and Mines [26], AuBe has a tetragonal lattice with $c/a = 1.01$.
** Diamond-type [26].
*** According to Chatterjee and Mines [26], $AuBe_5$ has a ZnS-type f.c.c. lattice with $a = 6.098$ Å.

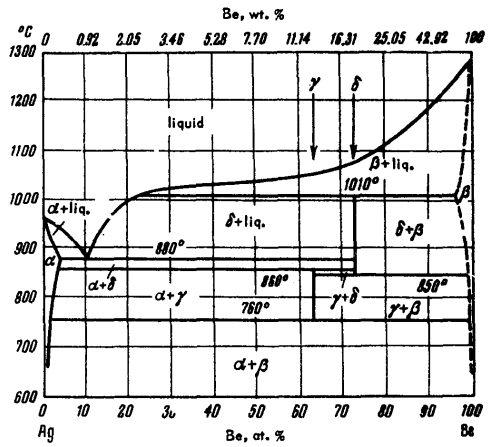

Fig. 2. Equilibrium diagram of the silver–beryllium system.

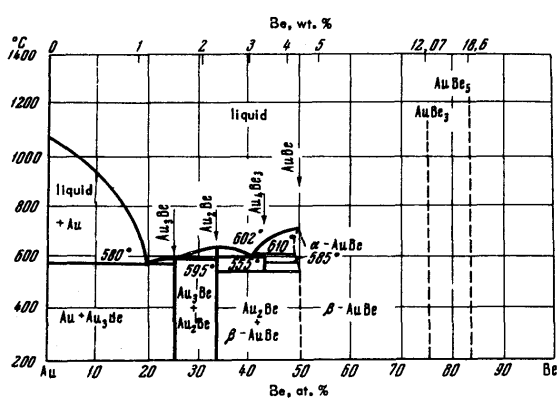

Fig. 3. Equilibrium diagram of the gold–beryllium system.

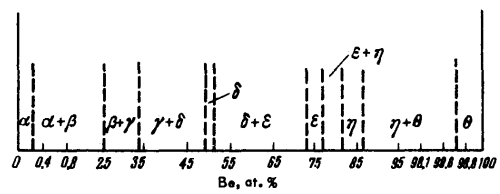

Fig. 4. Phase diagram of the gold–beryllium system.

Winkler, was not confirmed. The physical properties of the gold beryllides have not been studied much; it is known only that they exhibit great brittleness. Gold beryllides are usually prepared by powder metallurgical methods, particularly by hot pressing in a vacuum [31].

II. BERYLLIDES OF GROUP II METALS

A. BERYLLIDES OF MAGNESIUM AND THE ALKALINE EARTH METALS

Many attempts to alloy beryllium with magnesium [32,33] have failed, owing to the volatility of magnesium, and success was achieved [34,35] only by melting the metals in hydrogen under a pressure of ~ 100 atm. Later Baker and Williams [36] obtained $MgBe_{13}$, still the only compound of this system; it decomposes into the elements in a vacuum at 950°, and the authors showed that the eutectic between this compound and magnesium melts at a temperature very close to the melting point of magnesium [1,37]. Beryllium–magnesium alloys can be obtained by the methods of powder metallurgy [38] — either by impregnating a pressed blank of beryllium powder at 750° under argon, or by diffusion of magnesium from magnesium foil around a compact pressed from beryllium powder at 4.8 tf cm^2; the diffusion is also carried out at 750°.

Beryllium–calcium alloys have been obtained [32] heating solid beryllium with molten calcium; a beryllium–calcium compound $CaBe_{13}$ was observed. This compound

has been obtained[39] by the reduction of beryllium oxide with calcium and shown to be extremely stable.

Both the beryllides $MgBe_{13}$ and $CaBe_{13}$ are f.c.c., with parameters 10.166 and 10.312 Å respectively[36]. They are isomorphous with $NaZn_{13}$.[40]

There is no information about beryllides of strontium, barium, and radium.

B. BERYLLIDES OF METALS OF THE ZINC SUBGROUP

Beryllium–zinc alloys have not been obtained, owing to the high volatility of zinc, even in argon under pressure[11]. According to old information[41], beryllium does not dissolve in mercury and does not form an amalgam with it. It has been stated[42] that an amalgam was obtained at the mercury cathode on electrolysis of $BeCl_2$–NaCl mixtures; the possibility of the existence of the compound $BeHg_2$ is suggested in this work. It was established[43] that the solubility of beryllium in mercury rises from 1.10×10^{-6}% at 100° to 4.5×10^{-5}% at 800°. According to data given in a review[9], mercury had no action on a beryllium container in 330 h at 315°. There is no information about the interaction of beryllium and cadmium[44].

III. BERYLLIDES OF THE TRANSITION METALS

A. BERYLLIDES OF METALS OF SUBGROUP IIIa (THE RARE-EARTH ELEMENTS

In addition to lanthanum and the lanthanides, the rare-earth elements also include scandium and yttrium, which are close to the lanthanides as regards position in the Periodic System and physicochemical and geochemical features, although it is more correct to relate them to the *d* transition metals of the third and fourth periods.

Scandium beryllides. By sintering mixtures of fine scandium and beryllium (with 0.47% oxygen) powders at 1250° and then grinding the sinters and resintering, alloys of the Be–Sc system were obtained[45] in which from 0.5 at.% Sc onwards X-ray diffraction shows a phase with a structure of $NaZn_{13}$ type, isomorphous with the phases of analogous composition of yttrium and the lanthanides on the one hand, and of zirconium on the other. The melting point of $ScBe_{13}$ is above 1300°. Further investigation of the Be–Sc system[46,47] showed the presence of two more compounds; $ScBe_5$ and Sc_2Be_{17}, analogous to the corresponding beryllides of zirconium and hafnium.

Yttrium beryllides. In the Be–Y system, the diagram of which has been constructed by Lundin[48] (Fig. 5), there is one compound YBe_{13} with m.p. ~ 1920° and of $NaZn_{13}$-type structure[46,49]. Previously, the melting point of YBe_{13} had been taken as 1600° ± 300°.[50] The hardness of this compound is 870 kgf mm^{-2} (on the Knoop microhardness scale)[50,51], or 1240 kgf mm^{-2} from measurements[49] with a PMT-3 microhardness tester (100 g load). The compound is resistant to oxidation up to 1300°.[51]

Beryllides of the lanthanides. All the lanthanides form compounds MBe_{13} with beryllium[49,52,53]. Gladyshevskii and coworkers[53] obtained the beryllides MBe_{13} for all the lanthanides except Pm and Gd by melting

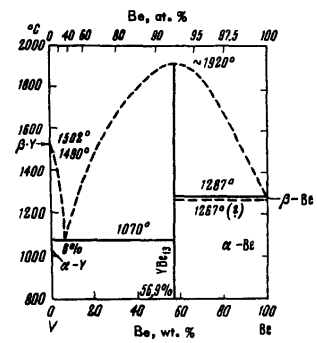

Fig. 5. Equilibrium diagram of the beryllium–yttrium system.

TABLE 2. Properties of the beryllides of the rare-earth metals.

Beryllide	Be, wt. %	Structure	Lattice parameters, Å		Density, g cm^{-3}	M.p., °C
			a	*c*		
$ScBe_5$	50.1	$CaCu_5$-type hex.	4.55[46,47]	3.50[44,45]	—	—
Sc_2Be_{17}	58.0	Th_2Ni_{17}-type hex.*	7.61[46]	7.50[44]	—	—
$ScBe_{13}$	72.4	$NaZn_{13}$-type cub.	10.10[47]	—	—	>1300
YBe_{13}	56.8	ditto	10.239[45,46—50]	—	2.57[47—50]	1920[46,50] 1600[51]
$LaBe_{13}$	45.8	»	10.43[57] 10.44[58] 10.457[47] 10.450[55]	—	2.79[57]	1720[57,59,60]
$CeBe_{13}$	45.6	»	10.375[40] 10.378[47,55]	—	2.81[57]	1720—1925[57]
$PrBe_{13}$	45.4	»	10.374[57] 10.367[55]	—	3.06[53]	—
$NdBe_{13}$	44.9	»	10.390[53] 10.356[55]	—	—	—
$PmBe_{13}$	44.8	»	10.33[55]	—	—	—
$SmBe_{13}$	43.9	»	10.325[53] 10.28[55]	—	—	—
$EuBe_{13}$	43.4	»	10.300[53] 10.288[55]	—	—	—
$GdBe_{13}$	42.9	»	10.27[55]	—	—	—
$TbBe_{13}$	42.3	»	10.254[53] 10.251[55]	—	—	—
$DyBe_{13}$	41.9	»	10.239[53] 10.240[55]	—	—	—
$HoBe_{13}$	41.6	»	10.225[53] 10.220[55]	—	—	—
$ErBe_{13}$	41.2	»	10.210[53,54] 10.20[54] 10.215[55]	—	—	—
$TuBe_{13}$	40.9	»	10.199[53] 10.192[55]	—	—	—
$YbBe_{13}$	40.6	»	10.182[53] 10.19[55,60]	—	—	—
$LuBe_{13}$	40.3	»	10.173[53] 10.177[55]	—	—	—

* Or Th_2Zn_{17}-type; and then the parameter is c = 11.25 Å (the two types are difficult to distinguish by X-rays).

distilled beryllium (99.8% purity) with metals of 95–99% purity in crucibles of BeO (or of Al_2O_3 lined with BeO) under argon in a Tammann furnace. An erbium beryllide of the same composition was obtained earlier[54]. Beryllides of a series of lanthanides were obtained[55] by reduction of the oxides with beryllium in a vacuum at 1300°:

$$M_2O_3 + 29Be = 2MBe_{13} + 3BeO.$$

Yttrium and lanthanum beryllides have been obtained[56] by sintering the metal powders with an excess of beryllium in tantalum crucibles at 1180° for 2 h in a vacuum of not below 5×10^{-6} mmHg followed by removal of the excess of beryllium by vacuum distillation at 1050° for 5 h.

In the same work the behaviour of YBe_{13} and $LaBe_{13}$ in a vacuum at temperatures up to 1550°K was investigated; it was found that the two compounds are appreciably dissociated above 1050° and equations were derived for the temperature dependence of the vapour pressure of beryllium over the beryllides during their thermal dissociation:

$$\text{for } YBe_{13}\text{: } \log P_{mm} = -\frac{16\,420}{T} + 8.30 \quad (1040\text{–}1290^\circ),$$

$$\text{for } LaBe_{13}\text{: } \log P_{mm} = -\frac{16\,600}{T} + 8.73 \quad (1080\text{–}1270^\circ).$$

Table 2 gives some information about the properties of beryllides of the rare-earth metals.

B. BERYLLIDES OF METALS OF SUBGROUP IVa

Titanium beryllides. Misch[23] obtained the compound $TiBe_2$ and showed that this beryllide crystallises in the $MgCu_2$ type. A systematic investigation of Be–Ti alloys was made by Erlich[62] on specimens obtained by sintering mixtures of titanium and beryllium powders, the sintering temperatures being: 1600° for alloys of empirical formula $TiBe_{0.4}$, 1300° for $TiBe_{0.5}$, and up to 1500° for $TiBe_{1.0}$ and alloys richer in beryllium. Erlich thinks that the composition $TiBe_{0.5}$ corresponds approximately to the eutectic of the system. X-Ray investigation of the alloys with empirical formulae from $TiBe_{0.1}$ to $TiBe_{10}$ showed that the solubility of beryllium in titanium is less than corresponds to the composition $TiBe_{0.1}$; the compounds have according to Erlich's results, the compositions TiBe, $TiBe_2$, $TiBe_4$, and $TiBe_{10}$, of which the first and the two last compounds have not been identified by X-ray diffraction. The compound TiBe evidently has a wide homogeneity region, since even the composition $TiBe_{0.75}$ gives an X-ray diagram identical with that of the alloy TiBe. The $TiBe_2$ phase has, according to Misch's data[23], a structure of $MgCu_2$ type with a parameter $a = 6.42_7$ Å, and this compound also has a certain region of homogeneity, since the determination of the lattice parameter of this phase in an alloy of conventional composition $TiBe_3$ gave a rather higher value, 6.45_6 Å. Later, $TiBe_{12}$[63] and Ti_2Be_{17}[58] were obtained directly from the elements; they are both hexagonal — the first of $ThMn_{12}$ type (sub-type $TiBe_{12}$ with 48 atoms in the unit cell) and the second of U_2Zn_{17} type. Later these phases were the subject of repeated investigations, which have been reviewed[64], and it is now accepted that $TiBe_{12}$ is not hexagonal but has a tetragonal structure of $ThMn_{12}$ type (analogous to the structures of VBe_{12} and $CrBe_{12}$), and that the Ti_2Be_{17} phase, which had been thought to be rhombohedral[65] or trigonal[66] is really hexagonal[64], with lattice parameters somewhat different from those found by Paine and Carrabine[58]. The $TiBe_{12}$ structure, as shown by Gillam and Rooksby[64] readily changes into the related Ti_2Be_{17} structure on loss of some of the beryllium atoms. The part of the diagram from Ti to $TiBe_2$ was studied[67] again in detail and the compounds TiBe and $TiBe_2$ were identified by X-ray diffraction; the general form of this part of the diagram was also confirmed. Hence the existence of at least four titanium beryllides, TiBe, $TiBe_2$, Ti_2Be_{17}, and $TiBe_{12}$, can now be considered established. Two of these are discounted in the hypothetical equilibrium diagram of the system constructed by the McQuillans[68] (Fig. 6), which now needs considerable modification.

Erlich[62] obtained titanium beryllides by sintering titanium and beryllium powders and also by arc melting in argon with a non-consumable tungsten electrode. According to Raub and Plate[20] the reaction between titanium and beryllium in powder mixtures starts at 800°. It is reported[69] that $TiBe_2$ is readily formed on heating briquettes, pressed from beryllium and titanium powders, in argon at 1200° for 1 h. $TiBe_2$ is also made by vacuum hot pressing[70] under a pressure of up to 100 kgf cm^{-2} in graphite dies coated with Al_2O_3.

Specimens of $TiBe_{12}$ with density 94%, obtained by vacuum hot pressing have high resistance to oxidation at 1260° for 100 h.[70] The high oxidation resistance of $TiBe_2$ and $TiBe_{12}$ has also been mentioned in a review[59].

Table 3 gives some information about the properties of titanium beryllides.

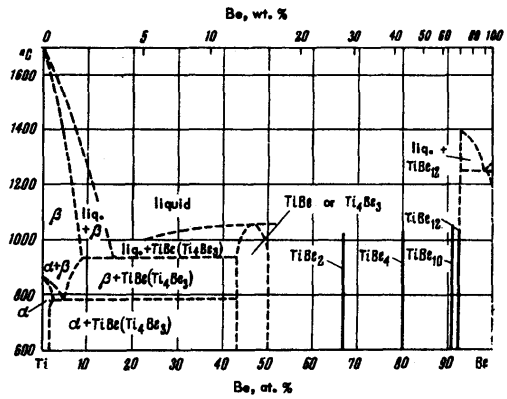

Fig. 6. Equilibrium diagram of the beryllium–titanium system.

TABLE 3. Properties of titanium beryllides.

Property	Beryllide			
	TiBe	$TiBe_2$	Ti_2Be_{17}	$TiBe_{12}$
Be content, wt. %	15.8	27.3	61.5	69.4
Structure	hex.	cub.	hex.	tetr.
Structural type	—	$MgCu_2$	U_2Zn_{17}	$ThMn_{12}$
Lattice parameters, Å				
a	3.20[64] 3	6.42[28,63,67] 7	7.35[64]*	7.36[64]**
c	3.69[64] 3	—	7.26	4.195
c/a	1.15	—	0.984	0.571
Density (X-ray), g cm^{-3}	—	—	—	2.28[70]
Melting point, °C	—	1800—1900	—	1427[70]
Gain in weight on oxidation at 1260° for 100 h, mg cm^{-2}	—	—	—	3.0[70]
Bend strength, kgf mm^{-2}				
1260°	—	—	—	7.8[59]
1370°	—	—	—	2.5
1510°	—	—	—	1.9
Limit of proportionality, kgf mm^{-2} (1260°)	—	—	—	1.4[59]
Superconductivity transition temperature, °K	—	<1.02[73]	—	—
Emissivity (at 800–1800°, $\lambda = 650$ μm)	—	0.73[73]	—	—

* See also Refs. 58, 65, 66, and 71.

** See also Refs. 63 and 65.

Zirconium beryllides. The first systematic investigation of beryllium–zirconium alloys was made by Hausner and Kalish[74] on specimens made by powder metallurgy. Lustman and Kerze[75] constructed the Be–Zr equilibrium diagram from the data of Hausner and Kalish[74], McGurty and coworkers[76], and others, but it was investigated again[77], from the results of which work Fig. 7 has been constructed. According to these results, the system contains the compounds $ZrBe_2$, $ZrBe_6$, and $ZrBe_9$, which are formed by peritectic reactions at 1235°, 1475°, and 1555° respectively, and $ZrBe_{13}$, which melts congruently at 1645°. Whereas the compositions of the beryllides $ZrBe_2$ [76-78] and $ZrBe_{13}$ [40,47] are accepted as the result of all the studies, the compositions of the beryllides with intermediate beryllium concentrations are at variance. Thus whereas some workers[76,77] take the composition of a beryllide as $ZrBe_6$ (evidently the most reliable), another[79] gives the composition as $ZrBe_5$. The beryllide of composition $ZrBe_9$, according to some[76,77] obviously corresponds to the most reliable composition Zr_2Be_{17}. Evidently, the composition $ZrBe_{16}$ given in one paper[76] is erroneous, and it obviously is the highest beryllide $ZrBe_{13}$ with beryllium impurity.

The zirconium beryllides Zr_2Be_{17} and $ZrBe_{13}$ — one of the most refractory of the transition metal beryllides (Table 4) — exhibit relatively high hardness; Fig. 8 shows the temperature dependence of the hardness of $ZrBe_{13}$.[59] There are marked differences in the hardness for $ZrBe_{13}$ obtained by different authors: 1650 kgf mm^{-2} according to Lewis[59], 790 kgf mm^{-2} according to Chubb and Dickerson[50], and 1130 kgf mm^{-2} according to Getz[79].

At high temperatures (~ 1400–1500°), Zr_2Be_{17} and $ZrBe_{13}$ show considerable resistance to oxidation[79,80], but over a certain temperature range they react rapidly with moisture, which leads to their rapid oxidation and disintegration into powder[81]. According to this work[81], hot-pressed $ZrBe_{13}$ showed this effect in the range 593–927°, but it is not observed below 538° nor above 982° in tests lasting 100 h. In this connection there have been several detailed investigations of the oxidation of $ZrBe_{13}$ in the medium-temperature range; they are cited in Getz' review[79]. In particular, it has been shown that the oxidation proceeds mainly inside the grain, although the oxidation products are partly liberated at the grain boundaries;

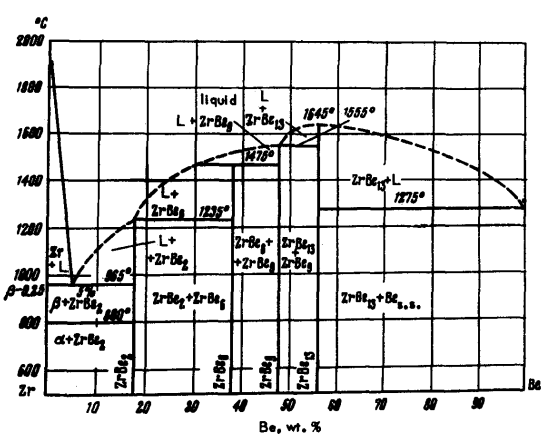

Fig. 7. Equilibrium diagram of the beryllium–zirconium system.

TABLE 4. Properties of zirconium beryllides.

Property	Beryllide			
	$ZrBe_2$	<$ZrBe_9$>	Zr_2Be_{17}	$ZrBe_{13}$
1	2	3	4	5
Be content, wt. %	16.5	33.0	45.6	56.3
Structure	hex.	hex.	rhombohedral	f.c.c.
Structural type	AlB_2	$CaZn_5$	U_2Zn_{17}	$NaZn_{13}$
Lattice parameters, Å				
a	3.82 [78]	4.564 [83]	7.548 [83]*	10.067 [40]
c	3.25	3.485	10.997	—
c/a	0.85	0.764	1.457	—
Density, g cm^{-3}	—	—	3.08 [79]	2.72 [51,79]
Melting point, °C	1200 [76]	1530 [76]	1980 [79]	1927 [79]
Vickers hardness at 20°, 2.5 kg load, kgf mm^{-2}			1750 [75,84]	2000 [51]
	—	—	1130 [79]	1000 [79]
	—	—	—	1650 [59]
Knoop hardness (50 g load), kgf mm^{-2}	—	—	—	790 [50,51]
Gain in weight in oxidation at 1260° for 100 h, mg cm^{-2}	—	—	—	7.8 [70]
Depth of oxidation after 100 h, mm				
1371°	—	—	0.0127 [79,80]	0.0127 [79,80]
1482°	—	—	0.0305 [79,80]	0.0330 [79,80]
Bend strength, kgf mm^{-2}				
20°	—	—	17.5 [75]	17.5 [79]
982°	—	—	16.1 [79]	12.6 [79]
1260°	12.1 [79]**	—	27.7 [59]	19.8 [59]
			28.0 [79]	28.0 [79]
1371°	5.2 [79]***	—	19.0 [59]	19.8 [59]
			28.0 [79]	26.0 [79]
1510°	—	—	17.2 [59]	12.6 [59]
			24.6 [79]	17.5 [79]
Young's modulus, kgf mm^{-2}				
20°	—	—	~33 500 [79]	~33 000 [79]
871°	—	—	~28 000 [79]	~28 000 [79]
1260°	—	—	18 300 [59]	14 100–28 100 [59]
1371°	—	—	10 500–21 100 [59,79]	14 000 [79,59]
1510°	—	—	7000 [59]	7000 [59]
Elongation in bending, %				
20°	—	—	0.1 [79]	0.05 [79]
871°	—	—	0.1 [79]	0.07 [79]
1371°	—	—	0.3 [79]	0.25 [79]
1510°	—	—	1.1 [79]	0.6 [79]
Limit of proportionality, kgf mm^{-2}				
1260°	—	—	16.4 [59]	1.4 [59]
1370°	—	—	7.1 [59]	3.3 [59]
1510°	—	—	2.6 [51]	—
Ultimate compressive stress, kgf mm^{-2}				
20°	—	—	—	133 [79]
871°	—	—	—	105 [79]
1371°	—	—	—	49 [79]
Impact strength, kgf cm^{-2}				
20°	—	—	—	< 1.15 [59]
				0.115 [57]
1095°	—	—	—	13.8 [85]
Resistance to thermal shock				
1260°	—	—	—	better than for MgO at 100° [59]
Heat capacity per unit mass, cal g^{-1} deg^{-1}				
538°	—	—	—	0.38 [79]
1482°	—	—	—	0.47 [79]
Thermal conductivity, cal s^{-1} cm^{-1} deg^{-1}				
760°	—	—	—	0.067 [57,59]
1370°	—	—	—	0.085 [57,59]
1385°	—	—	—	0.082 [59,84]
1482°	—	—	—	0.0869 [79]
Coefficient of thermal expansion (× 10^6), deg^{-1}	—	—	8.39 [79]	9.86 [79]
Electrical resistivity, μΩ cm				
27°	—	—	—	16.4 [79]
649°	—	—	—	76.9 [79]
1260°	—	—	—	100.4 [79]
Vapour pressure (× 10^8), mmHg				
1260°	—	—	1.4 [82]	—
1371°	—	—	11.3 [82]	—

* For a pseudocubic cell a = 5.69 Å.

** For $ZrBe_9$.

*** For "Zr_2Be_{13}".

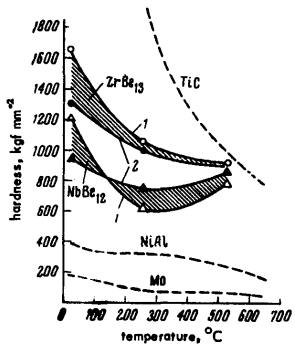

Fig. 8. Temperature dependence of hardness for some beryllides and other heat-resistant materials. Load: 1) 26 g; 2) 100 g.

TABLE 5. Properties of hafnium beryllides.

Property	Beryllide			
	$HfBe_2$	$HfBe_5$	Hf_2Be_{17}	$HfBe_{13}$
Be content, wt. %	9.18	20.2	29.9	39.7
Structure	hex.	hex.	hex.	cub.
Structural type	AlB_2	$CaZn_5$	U_2Zn_{17}	$NaZn_{13}$
Lattice parameters, Å				
a	3.788 [86]	4.534 [86]	7.499 [86]	10.010 [86]
c	3.168	3.471	21.905	—
c/a	0.836	0.765	2.921	—
Microhardness (100 g load), kgf mm^{-2}	980 [86,87]	1340 [86,87]	1085 [86,87]	1200 [86,87]
Knoop microhardness, kgf mm^{-2}	77 [87] *	87 [87] **	98 [87] ***	—
Melting point, °C	1273 [87] *	1270 [87] **	1486 [87] ***	—

* For the alloy with 10.0 wt.% Be.
** For the alloy with 20.0 wt.% Be.
*** For the alloy with 33.0 wt.% Be.

the stresses created by the formation of the oxides can bring about the destruction of the beryllides. That this takes place in the medium-temperature region is compared with the fact that at 984–1093° $ZrBe_{13}$ partly loses beryllium, being converted into Zr_2Br_{17} (a layer of which is situated between the $ZrBe_{13}$ and the oxide layer)[81], which has a thermal expansion coefficient quite different from that of $ZrBe_{13}$. The addition of 0.35–0.45 wt.% Al to $ZrBe_{13}$ brings about a sharp rise in its oxidation resistance in the middle-temperature region, both in dry and in moist (dew point 14°) air, at the cost of some deterioration in high-temperature strength, and a marked increase in room-temperature strength. It was shown in this work that aluminium is very slightly soluble in $ZrBe_{13}$ and much more soluble in Zr_2Be_{17}, with which is evidently also connected the beneficial effect of the additions of aluminium on the oxidation resistance of the beryllide $ZrBe_{13}$ in the middle-temperature region. The rate of oxidation of zirconium beryllides obeys a logarithmic law[59,81], which agrees with the protective nature of the oxide film.

According to Bookhand and others[82] the vapour pressure above Zr_2Be_{17} at 1200–1400° is relatively low, $\sim 10^{-3}$ mmHg.

Zirconium beryllides can be made by powder metallurgy methods, either by sintering previously compacted mixtures of beryllium and zirconium powders[74] in argon (the reaction between zirconium and beryllium is reported[20] to start at 685°) or by hot pressing[76] at 1600–1800°.

Beryllium–zirconium alloys have been made[77] by fusing the components in an argon arc furnace; a similar method has been described[51] for $ZrBe_{13}$.

The same work[51] describes various methods for making articles from $ZrBe_{13}$ and some other beryllides ($NbBe_{12}$, $MoBe_2$) — in particular, by vacuum (~ 0.1 mmHg) hot pressing of mixtures of powders (200 mesh), the temperature being raised to 1500° over a period of 2–3 h, and then held at 1550–1600° for 1–2 h (all the regimes are quoted for cylindrical articles with a diameter and height of ~ 50 mm). Good results are also obtained by using casting (induction heating) and extrusion at $\sim 1620°$.

Hafnium beryllides. The beryllium–hafnium system is quite similar to the beryllium–zirconium system; the existence of four compounds in it has also been established[58,65,86–88]: $HfBe_2$, $HfBe_5$, Hf_2Be_{17}, and $HfBe_{13}$. The beryllide $HfBe_2$ has a hexagonal lattice of the AlB_2 type; $HfBe_5$ also has a hexagonal lattice, of the $CaZn_5$ type; the Hf_2Be_{17} phase is reported[65] to have two modifications: α-Hf_2Be_{17}, rhombohedral ($a = 7.494$, $c = 10.93$ Å), and β-Hf_2Be_{17}, hexagonal ($a = 7.44$, $c = 7.38$ Å), but others state[86,87] that there is only a hexagonal type of Nb_2Be_{17} identical in type with U_2Zn_{17} or Th_2Zn_{17}. Finally, $HfBe_{13}$ has a cubic structure of $NaZn_{13}$ type[87]. This work[87] drew attention to the fact that the lattice parameters of the hafnium beryllides are less than those of the corresponding zirconium phases; this is connected with the atomic radius of hafnium (1.59 Å) being less than that of zirconium (1.60 Å). The main information on the properties of the hafnium beryllides is given in Table 5.

According to these data[87] as the proportion of beryllium in the compounds with hafnium is increased, the distance between its atoms diminishes ($HfBe_2$ 2.179, $HfBe_5$ 2.17, Hf_2Be_{17} 2.14, $HfBe_{13}$ 2.07 Å) but the distance between the hafnium atoms increases, which indicates an increase in the covalency of the bond between the beryllium atoms.

Hafnium beryllides can be obtained either by melting the components together under argon in a high-frequency (beryllium-rich) or arc (hafnium-rich) furnace[86,87] or by powder metallurgy methods, especially by hot pressing of mixtures of the powders[88] followed by annealing.

C. BERYLLIDES OF METALS OF SUBGROUP Va

Vanadium beryllides. Misch[23] found the existence of the beryllide VBe_2 with a hexagonal lattice of $MgZn_2$ type and parameters $a = 4.385$, $c = 7.130$ kX, $c/a = 1.639$, with four molecules in the unit cell. Further investigations of the compounds in this system[89–91] confirmed the existence of VBe_2 and its structure, and also showed the compound VBe_{12} with a tetragonal lattice of $ThMn_{12}$ type.

The icosahedral configuration of the beryllium atoms in this structure and also the decrease in the distance between the beryllium atoms on going from VBe_2 (2.25 kX) to VBe_{12} (2.19 kX) shows a considerable proportion of covalency in the bond between the beryllium atoms.

The existence of VBe_{12} was further confirmed by Batchelder and Raeuchle[92], who gave values of the lattice parameters for single crystals which were different from those quoted[89–91].

Vanadium beryllides are obtained by melting the components together in quartz containers in a resistance furnace under argon (Table 6).

Niobium beryllides. In the Be–Nb system the existence of a compound $NbBe_{12}$ with a face-centred tetragonal lattice was established[86,87,92] and then rhombohedral Nb_2Be_{17} was observed[93]. In addition there have been reports of the existence of $NbBe_2$,[91,94] Nb_3Be_2,[95] $NbBe_5$,[91,96] of which $NbBe_2$ and $NbBe_5$ were accepted in the construction of a tentative variant[96] of the Be–Nb equilibrium diagram (Fig. 9). This diagram, which has been described in detail[96,97] was confirmed by additional investigation[98] and it was shown that the solid solubility of niobium in beryllium is very small (considerably less than 0.7 wt.% Nb), eutectic crystallisation of α-Be + $NbBe_{12}$ from the melt takes place at 2.5 wt.% Nb, and the eutectic temperature is close to the melting point of pure beryllium. Furthermore, it is stated that the phase $NbBe_{12}$ may not be formed as a compound with an open maximum melting point but by a peritectic reaction between the melt and compound Nb_2Be_{17}, which obviously throws doubt on the part of the diagram in Fig. 9 between the phases Nb_2Be_{17} and $NbBe_{12}$; this part requires further, more detailed investigation.

In a thermal diffusion study of the beryllium–niobium system[96] the temperature dependence of the diffusion coefficients was determined approximately for "$NbBe_8$" (Nb_2Be_{17}) and $NbBe_{12}$:

$$D_{\text{«NbBe}_8\text{»}} = 5.7\times10^{-9}\exp(-14\,740/RT),$$

$$D_{NbBe_{12}} = 7.66\times10^{-4}\exp(-32\,000/RT)$$

TABLE 6. Properties of vanadium beryllides.

Property	Beryllide	
	VBe_2	VBe_{12}
Be content, wt. %	26.2	68.2
Structure	tetr.	tetr.
Structural type	$MgZn_2$	$ThMn_{12}$
Lattice parameters, Å		
a	4.394[88]	7.278[92]*
c	7.144	4.212
c/a	1.639	0.579
Density, g cm^{-3}	—	2.37[92]

* According to other results[88–91], a = = 7.266 Å, c = 4.195 Å, c/a = 0.577.

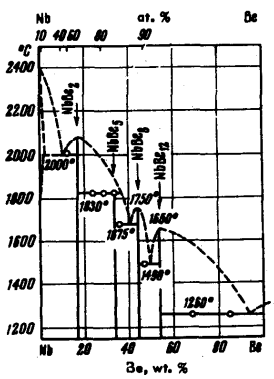

Fig. 9. Equilibrium diagram of the beryllium–niobium system.

A review of the data on the oxidation resistance of beryllium–niobium alloys has been given in a monograph[97]; that of the niobium beryllides proper has been investigated[59,79]. The moderate oxidation resistance of the beryllide $NbBe_2$ and its alloys with niobium was demonstrated[97]; the beryllides $NbBe_5$ and especially Nb_2Be_{17} and $NbBe_{12}$ are stable to oxidation, but the effect of a diminution in this stability in the middle temperature region noted for the higher beryllides of zirconium also occurs with the niobium beryllides, but is not so sharply expressed[79].

The niobium beryllides have relatively high hardness, which increases with the beryllium concentration[96–98]; Fig. 8 shows the temperature dependence of the hardness of $NbBe_{12}$ (data taken from Lewis[59]), the hardness minimum at 290° is still unexplained. The strength of the

TABLE 7. Properties of niobium beryllides.

Property	Beryllide			
	$NbBe_2$	$NbBe_5$	Nb_2Be_{17}	$NbBe_{12}$
Be content, wt. %	16.2	32.7	45.3	54.0
Structure	hex.	hex.	rhombohedral	tetr.
Structural type	—	—	Th_2Zn_{17}	$ThMn_{12}$
Lattice parameters, Å				
a	4.465[96]	—	5.599[93]	7.376[92]
c	7.302	—	α = 82.84°	4.258
c/a	0.628	—	—	0.577
Density, g cm^{-3}	—	—	3.28[93]	2.88[92]
Melting point, °C	2080[97]	~1900[97]	1750[97]*	1650[97]
			1704[79]	1700[59,79]
Heat of formation, kcal mole^{-1}	14.6±1.9[97]	46.4±3.8[97]	20.5±2[97]*	29.8±9.6[99]
Heat capacity per unit mass, cal g^{-1} deg^{-1}				
538°	—	—	—	0.39[75]
1482°	—	—	—	0.44[79]
Thermal conductivity, cal cm^{-1} s^{-1} deg^{-1}				
760°	—	—	0.0778[79]	0.0723[79]
1482°	—	—	0.0819[79]	0.0785[79]
Coefficient of thermal expansion (× 10^6) (27–1510°), deg^{-1}	—	—	8.83[79]	9.36[79]
Electrical resistivity, μΩ cm				
27°	—	—	—	55.6[79]
649°	—	—	—	166.7[79]
1260°	—	—	—	~200[79]
Microhardness, kgf mm^{-2}	—	—	1400[96]	1200[96]
			1430[98]	1900[96]
			1000[57]	1200[59]
Knoop hardness (50 g), kgf mm^{-2}	—	—	—	1100[51]
Vickers hardness	—	—	1060[98]	~480[98]
	—	—	1000[79]	500[79]
Young's modulus, kgf mm^{-2}				
20°	—	—	30100[79]	33 000[79]
871°	—	—	~28000[79]	28 000[79]
1260°	—	—	15500[59]	21 100[59]
1370°	—	—	~17500[79]	17 500[79]
			9800[59]	14 800[59]
1510°	—	—	—	14 100[59]
Bend strength, kgf mm^{-2}				
20°	—	—	21.7[79]	13.4[79]
982°	—	—	24.5[79]	10.5[79]
1260°	—	—	49.1[79]	31.5[79]
			27.4[59]	26.3[59]
1370°	—	—	44.2[79]	31.5[79]
			26.4[59]	25.4[59]
1510°	—	—	25.2[79]	13.4[79]
			11.5[59]	14.3[59]
Elongation in bending, %				
20°	—	—	0.1[79]	0.1[79]
871°	—	—	0.15[79]	0.1[79]
1370°	—	—	2.0[79]	1.0[79]
1510°	—	—	~7[79]	2.2[79]
Limit of proportionality, kgf mm^{-2}				
1260°	—	—	6.6[59]	—
1370°	—	—	2.5[59]	—
Ultimate compressive stress, kg mm^{-2}				
20°	—	—	—	140[79]
871°	—	—	—	91[79]
1370°	—	—	—	56[79]
Impact strength, kgf cm^{-2}				
20°	—	—	—	<1.15[96]
				0.115[57]
1260°	—	—	—	27.6[55]
Depth of oxidation after 100 h, mm				
1370°	—	—	0.01525[79]	0.0229[79]
1482°	—	—	0.0483[79]	0.0508[79]
Gain in weight in oxidation at 1260° for 100 h, mg cm^{-2}	—	—	2.6[70]	1.7[70]

* For "$NbBe_8$".

niobium beryllides is of the same order as that of the beryllides of other transition metals but at high temperatures the strength is somewhat higher than that of other beryllides. The heats of formation of all the beryllides shown in Fig. 9 and the temperature dependence of the diffusion coefficients for Be in Nb with formation of beryllide phases have been determined[96]. Table 7 summarises the properties of the niobium beryllides.

The niobium beryllides can be made by the methods of powder metallurgy[59,91]. Cherkashin and coworkers[91] sintered mixtures of the powders at 1000° in a protective medium (molten sodium chloride) for 5–24 h, followed by long (10 days) annealing at 400°. However, it is more customary to obtain them by melting the components together, for example, under argon in a high-frequency furnace[98].

TABLE 8. Properties of the highest tantalum beryllides.

Property	Beryllide	
	Ta_2Be_{17}	$TaBe_{12}$
Be content, wt. %	29.7	37.6
Structure	rhombohedral	tetr.
Structural type	Th_2Zn_{17}	$ThMn_{12}$
Lattice parameters, Å		
a	7.388[58,65]	7.334[92,100]
c	10.74	4.267
c/a	1.458	0.582
Density, g cm^{-3}	5.05[79]	4.18[92]
Melting point, °C	1988[79]	1850[59,79]
	1980[59]	
Microhardness, kgf mm^{-2}	1120[58,79]	—
Vickers hardness, H_v (load 2.5 kg)	1120[79]	729[79]
Young's modulus, kgf mm^{-2}		
20°	35000[79]	18 900[79]
871°	~28000[79]	23 200[79]
1260°	12000[59]	16 900[59]
1370°	~14000[79]	23 800[79]
	9100[59]	9800[59]
1510°	7000[59]	7000[59]
Bend strength, kgf mm^{-2}		
20°	21.0[79]	21.7[79]
982°	28.1[79]	—
1260°	54.7	37.2[79]
1370°	39.3[79]	30.2[79]
	—	25.3—37.4[59] *
1480°	—	4.5 **
1510°	24.6[79]	18.2[79]
		18.6[59]
Elongation in bending, %		
20°	0.1[79]	0.1[79]
871°	0.2[79]	0.1[79]
1371°	2.6[79]	1.1[79]
1510°	~5[79]	2.6[79]
Limit of proportionality, kgf mm^{-2}		
1370°	—	2.5—13.0[59]
1510°	—	2.5[59]
Ultimate compressive stress, kgf mm^{-2}		
20°	—	~105[79]
871°	—	133[79]
Depth of oxidation after 100 h, mm		
1371°	0.0076[79]	0.0127[79]
1482°	0.0229[79]	0.0229[79]
1649°	0.0763[82] ***	—
704°	0.00025[82]	—
871°	0.00125[82]	—
Gain in weight during oxidation at 1260° for 100 h, mg cm^{-2}	—	18.0[70]
Vapour pressure (× 10^3), mmHg		
1260°	1.7[82]	—
1366°	5.6[82]	—
1371°	5.2[82]	—
Heat capacity per unit mass, cal g^{-1} deg^{-1}		
538°	0.22[79]	0.27[79]
1482°	0.26[79]	0.30[79]
Thermal conductivity, cal s^{-1} cm^{-1} deg^{-1}		
760°	0.0715[78]	0.0732[79]
1482°	0.0781[79]	0.0897[79]
Coefficient of thermal expansion (27–1510°) (× 10^6), deg^{-1}	8.72[79]	8.42[79]
Electrical resistivity, μΩ cm		
27°	—	43.5[79]
649°	—	111.2[79]
1260°	—	133.4[79]

* For grain size 12 μm.
** For grain size 45 μm.
*** 10 h.

Tantalum beryllides. The investigation of alloys of beryllium and tantalum was started by Kaufmann and coworkers[11], and later Gladyshevskii and Kripyakevich[100] found the compound $TaBe_{12}$ with a tetragonal structure of $ThMn_{12}$ type (a = 7.322, c = 4.247 kX); simultaneously the same compound was established in another study[92]. Later, the compounds Ta_2Be, $TaBe_2$, Ta_3Be_2, $TaBe_3$, and Ta_2Be_{17} were reported[58,65,179]. The properties of the higher beryllides Ta_2Be_{17} and $TaBe_{12}$ have been studied best — they are refractory compounds with m.p. 1900–2000°, resistant to oxidation; unlike the zirconium and niobium beryllides, the tantalum beryllides are not subject to catastrophic oxidation in the middle-temperature region[79]. At high temperatures Ta_2Be_{17} has a vapour pressure of the same order as metallic beryllium[82]. Information about the properties of the lower tantalum beryllides is limited to what is known about their crystal structure[65]. $TaBe_2$ is cubic with lattice parameter a = 6.51 Å, Ta_3Be_2 is tetragonal with a = 6.5, c = 3.32 Å, $TaBe_3$ is rhombohedral with a = 4.53, c = 20.95 Å. The melting point of $TaBe_{12}$ is 1845° and its density 9.79 g cm^{-3}.[57] Table 8 gives the properties of the higher tantalum beryllides. The Be–Ta equilibrium diagram has not been studied.

Tantalum beryllides are obtained predominantly by powder metallurgy methods[59,100].

D. BERYLLIDES OF METALS OF SUBGROUP VIa

Chromium Beryllides. The diagram of the Be–Cr system was constructed by Edwards and Johnstone[101] up to 30 wt.% Be and shows the existence of a beryllide of composition $CrBe_2$ (Fig. 10), which had been found even earlier and identified by X-ray diffraction[23,102]. $CrBe_2$ is a phase of variable composition, homogeneous (according to Cherkashin and coworkers[91]) in a region extending at least from 70.9 to 77.5 at.% Be. A second compound has been established[90–92]: $CrBe_{12}$, which exists in a narrow concentration region at beryllium concentrations close to 92 at.%.[91] This compound is denoted by the symbol X in Fig. 10. Table 9 gives information about the properties of the chromium beryllides.

Chromium beryllides have been made by melting the components in pure argon[91,101]; they can also be obtained successfully by powder metallurgy[59].

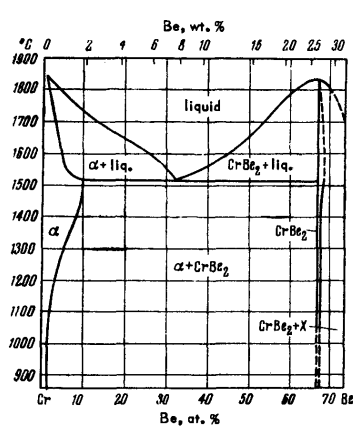

Fig. 10. Equilibrium diagram of the beryllium–chromium system.

TABLE 9. Properties of chromium beryllides.

Property	Beryllide	
	$CrBe_2$	$CrBe_{12}$
Be content, wt. %	25.8	68.1
Structure	hex.	tetr.
Structural type	$MgZn_2$	$ThMn_{12}$
Lattice parameters, Å		
a	4.259 [101]	7.234 [89—91]
c	6.975	4.176
c/a	1.638	0.577
Density, g cm^{-3}	4.34 [89]	2.44 [89]—2.51 [91]
Melting point, °C	1845 [101]	—
	1840 [59]	
Emissivity (λ = 650 nm, 800—1800°)	0.76 [73]	—
Microhardness, kgf mm^{-2}	1288 [59]	—
Gain in weight on oxidation at 1260° for 100 h, mg cm^{-2}	2.4 [70]	—

Molybdenum beryllides. Only the molybdenum-rich part of the Be–Mo diagram (up to 7 wt.% Be) has been constructed [1]. The existence of two compounds in the system has been rather reliably established: $MoBe_2$ [23,103] and $MoBe_{12}$ [89,91,100,104]; in one work [103] the latter was given the composition $MoBe_{13}$, but this was later corrected by Raeuchle and Batchelder [104] and also by Gladyshevskii and Kripyakevich [100], who confirmed the composition $MoBe_{12}$. Furthermore, there is proof [58] of the compound Mo_3Be with a cubic structure of type O_h^3 with a = 4.89 Å and also a compound richer in beryllium $MoBe_{20}$ with structure $O_h^7(T_h^7)$ and a = 11.64 Å. A later investigation [105] confirmed the existence of this phase, but its composition was described by the formula $MoBe_{22}$ (instead of $MoBe_{20}$) with a structure of $ZrZn_{22}$ type, parameter a = 11.634 Å. The compounds Mo_3Be and $MoBe_{22}$ have hardly been studied, therefore Table 10 gives the properties for $MoBe_2$ and $MoBe_{12}$ alone.

Molybdenum beryllides can be made by melting the components in BeO crucibles under argon in a high-frequency furnace [100] and also by powder metallurgy [59]. The diffusion reaction of beryllium in molybdenum has been investigated [106] and it was shown that the phases $MoBe_2$, $MoBe_{12}$, and $MoBe_{22}$ are formed: $MoBe_2$ predominates up to 1000°, a mixture of $MoBe_2$ and $MoBe_{12}$ from 1000° to 1150°, and the phase $MoBe_{22}$ appears at higher temperatures. The layer on molybdenum consists successively of

TABLE 10. Properties of molybdenum beryllides.

Property	Beryllide	
	$MoBe_2$	$MoBe_{12}$
Be content, wt. %	17.4	53.2
Structure	hex.	tetr.
Structural type	$MgZn_2$	$ThMn_{12}$
Lattice parameters, Å		
a	4.442 [103]	7.271 [104]
c	7.356	4.234
c/a	1.658	0.585
Density, g cm^{-3}	5.92 [103]	3.02 [55]
	6.12 [59]	—
Melting point, °C	1840 [59]	~1700 [59],
Microhardness, kgf mm^{-2}	—	950 [57,58]
Young's modulus, kgf mm^{-2}		
1260°	—	10 500 [59]
1370°	—	8400 [59]
1510°	—	700 [59]
Gain in weight on oxidation at 1260° for 100 h, mg cm^{-2}	2.6	—

TABLE 11. Properties of the tungsten beryllides.

Property	Beryllide		
	WBe_2	WBe_{12}	WBe_{22}
Be content, wt. %	8.95	37.3	52.1
Structure	hex.	tetr.	cub.
Structural type	$MgZn_2$	$ThMn_{12}$	$ZrZn_{22}$
Lattice parameters, Å			
a	4.446 [23]	7.362 [92]	11.631 [58,105]
c	7.289	4.216	—
c/a	1.63	0.573	—
Density, g cm^{-3}		4,25 [92]	
Microhardness, kgf mm^{-2}	2188 [107]	1145 [107]	1080 [107] *

* For "WBe_{24}".

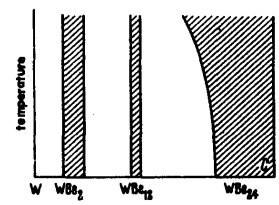

Fig. 11. Equilibrium diagram of the beryllium–tungsten system.

beryllide phases from the lowest beryllides to the highest; the diffusion proceeds preferentially through the beryllide layers.

Tungsten beryllides. In the beryllium–tungsten system, analogous to the beryllium–molybdenum system, the existence of the following beryllide phases has been established with sufficient reliability: WBe_2, [23,91,178] WBe_{12}, [91,62,100] and WBe_{22}, [58,105], the main properties of which are given in Table 11. Thermal diffusion has been investigated [107] in the Be–W system, the formation of three phases being established: WBe_2, WBe_{12}, and WBe_{24}; the last is evidently identical with the phase WBe_{22} which has been well identified by X-ray diffraction. According to the results, all three phases have homogeneity regions: the widest is the "WBe_{24}" phase, WBe_2 is narrower, and WBe_{12} is the narrowest (Fig. 11). The temperature dependence of diffusion coefficient in each phase has been determined approximately:

$$D_{WBe_2} = 1.10\times10^{-4}\exp(-3315/RT),$$
$$D_{WBe_{12}} = 2.36\exp(-66\,950/RT),$$
$$D_{\langle WBe_{24}\rangle} = 1.175\times10^{-3}\exp(-33\,800/RT).$$

It is reported [20] that on heating a compacted mixture of tungsten and beryllium powders, reaction between them to form intermetallic compounds begins at 880°; in the diffusion interaction of beryllium powder with the compact metal at 1100° for 4 h, all the beryllide phases are formed [107].

E. BERYLLIDES OF METALS OF SUBGROUP VIIa

Manganese beryllides. The solubility of beryllium in manganese is low [11,108]. According to some [23,93] there is a beryllide $MnBe_2$ of variable composition of $MgZn_2$ structure type; this structure type was also described by Hume-Rothery and Raynor [109]. A second compound [89,91]

TABLE 12. Properties of manganese beryllides.

Property	Beryllide		
	$MnBe_8$	$MnBe_6$	$MnBe_{12}$
Be content, wt. %	25.4	55.9	66.8
Structure	hex.	cub.	tetr.
Structural type	$MgZn_2$	$MgCu_2$	$ThMn_{12}$
Lattice parameters, Å			
a	4.239 [93]	5.931 [91]	7.276 [93]
c	6.923	—	4.256
c/a	1.632	—	0.585
Density, g cm^{-3}	—	—	2.40 [93]

has the composition $MnBe_8$ (at 400°) with a homogeneity region which broadens with temperature (at 1100° this region extends from $MnBe_8$ to $MnBe_{13}$); this beryllide has a cubic lattice of $MnCu_2$ type. Batchelder and Raeuchle [93] found the presence of a third beryllide $MnBe_{12}$.

It has been shown [20] that the reaction between compacted manganese and beryllium powders starts at 800°; the beryllides $MnBe_2$ and $MnBe_8$ have been obtained [91] by melting the components in a quartz container under argon. Table 12 gives information on the properties of manganese beryllides.

Technetium beryllides. There is no information about technetium beryllides.

Rhenium beryllides. According to Misch [23], the beryllium–rhenium system contains the compound $ReBe_2$; a beryllium-rich phase, which has been ascribed the composition $ReBe_{20}$, has been found [56]. It is evident that the true composition of this phase is $ReBe_{22}$, analogous to the corresponding phases of molybdenum and tungsten [105], with a cubic structure of the $ZrZn_{22}$ cubic type, lattice parameter [56] a = 11.64 Å.

The composition of the phase $ReBe_{22}$ has been established [110]; this beryllide is made by heating mixtures of rhenium and beryllium powders (in stoichiometric proportions) in BeO crucibles at 1650° for ~5 min under argon at a pressure of 0.5 atm. The lattice parameter is a = = 11.561 Å. In this beryllide the beryllium atoms form a complex skeletal polyhedron.

The beryllide $ReBe_2$ has a hexagonal lattice of $MgZn_2$ type with a = 4.354, c = 7.101 Å, c/a = 1.631. [23] $ReBe_2$ is prepared by heating pressed mixtures of the powders of the components under argon at 1200° and melts at a temperature above 2000°. The emissivity of $ReBe_2$ at 800–1600° (λ = 650 nm) is 0.80. [73]

F. BERYLLIDES OF METALS OF GROUP VIII

1. Beryllides of Metals of the Iron Group

Iron beryllides. The equilibrium diagram of the beryllium–iron system, constructed from published information [111,112] is shown in Fig. 12. Three beryllides exist in the system: $FeBe_2$, [113,114] $FeBe_8$, [113,114] and $FeBe_{12}$. [92,114] The beryllide $FeBe_2$ has high hardness and is ferromagnetic [112] with a Curie point at 643°.

The phases $FeBe_2$ and $FeBe_8$ have wide homogeneity regions [114], the $FeBe_{12}$ phase according to previous data [114] has the composition $FeBe_{12}$ and a hexagonal structure, although Batchelder and Raeuchle [92] conclusively confirmed its composition as $FeBe_{12}$ and a face-centred tetragonal structure.

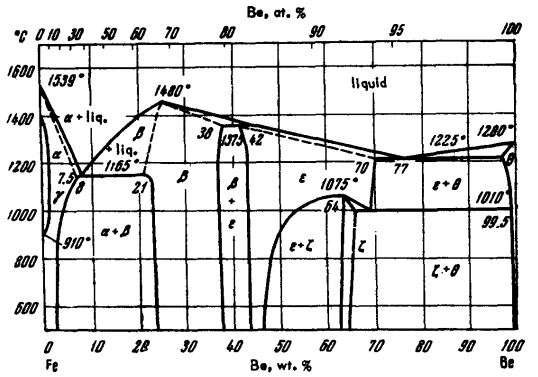

Fig. 12. Equilibrium diagram of the beryllium–iron system.

Table 13 gives the main information about the properties of the iron beryllides. The maximal solubility of Fe in Be is 0.0092 at.% (5.46 wt.%) at the eutectic temperature 1225°. [115]

Cobalt beryllides. After Köster and Schmid [116] who worked out the part of the Be–Co diagram up to 10 wt.% Be, Venturello and Burdese proposed the complete diagram of this system (Fig. 13). [117] In accordance with this diagram, the system contains the compounds CoBe [23,117,118] and Co_5Be_{21}, [117] however, according to Batchelder and Raeuchle [92] the lines of the X-ray diagram of this phase can

TABLE 13. Properties of the iron beryllides.

Property	Beryllide		
	$FeBe_2$	$FeBe_8$	$FeBe_{12}$
Be content, wt. %	24.5	44.6	66.3
Structure	hex.	cub.	tetr.
Structural type	$MgZn_2$	$MgCu_2$	$ThMn_{12}$
Lattice parameters, Å			
a	4.212 [113]	5.878 [113]	7.253 [92]
c	6.834	—	4.232
c/a	1.62	—	0.583
Density, g cm^{-3}	4.65 [113]	3.272 [114]	2.45 [89]
Melting point, °C	1480 [111,113]	~1375 [111,113]	~1300 [111,113,114]

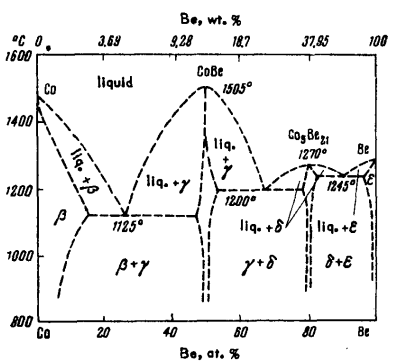

Fig. 13. Equilibrium diagram of the beryllium–cobalt system.

TABLE 14. Properties of the cobalt beryllides

Property	Beryllide		
	CoBe	$CoBe_5$	$CoBe_{12}$
Be content, wt. %	13.26	43.4	65.1
Structure	b.c.c.	f.c.c.	tetr.
Structural type	CsCl	$MgCu_2$	$ThMn_{12}$
Lattice parameters, Å			
a	2.615 [118]	5.852 [93]	7.237 [93]
c	—	—	4.249
c/a	—	—	0.587
Density, g cm^{-3}	—	—	2.49 [93]
Melting point, °C	1505	—*	—

* The melting point of the "Co_5Be_{21}" phase is reported [117] to be 1270°.

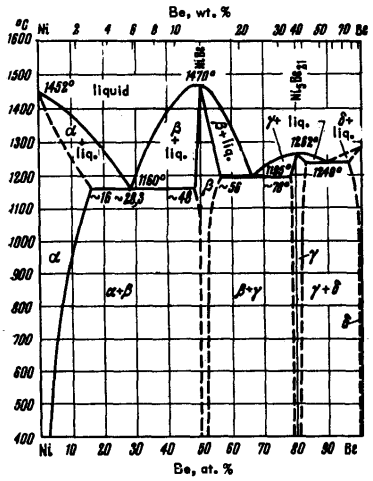

Fig. 14. Equilibrium diagram of the beryllium–nickel system.

be ascribed to $CoBe_{12}$ and $CoBe_5$, analogous to the corresponding iron beryllides, which seems more probable. CoBe is reported [23] to have an ordered b.c.c. lattice and Co_5Be_{21} has been investigated repeatedly [1,15,16]; Jahn [119] has given its equilibrium diagram in the most complete form (Fig. 14). nents under inert gas in an electric resistance furnace. Table 14 gives the main properties of the cobalt beryllides.

On heating mixtures of beryllium and cobalt powders, reaction between them starts at 670°. [20]

Nickel beryllides. The beryllium–nickel system has been investigated repeatedly [1,15,16]; Jahn [119] has given its equilibrium diagram in the most complete form (Fig. 14). According to this diagram the system contains the compounds NiBe and Ni_5Be_{21}, which have not very wide homogeneity regions and melt congruently. The maximal solubility of nickel in beryllium is 4.93 at.% at the eutectoidal temperature, 1065°. [115] The existence of Ni_5Be_{21} is probably doubtful (as is the analogous compound in the Be–Co system) but there have been no investigations in this direction and a phase of this composition has to be accepted at present. The structures of NiBe and Ni_5Be_{21} were investigated by Misch [113] and by Losana and Goria [120] and the results of the latter workers are considered [1] to be the most reliable data on the lattice parameters. The NiBe

TABLE 15. Properties of nickel beryllides.

Property	Beryllide	
	NiBe	Ni_5Be_{21}
Be content, wt. %	13.31	39.21
Structure	b.c.c.	cub.
Structural type	CsCl	Ni_5Zn_{21} (γ-brass)
Lattice parameter, Å		
a	2.621 [120]	7.625 [120]
Melting point, °C	1472 [119]	1262 [119]

phase is responsible for the precipitation hardening during the aging of Be–Ni alloys [121]. Beryllium–nickel alloys are made by melting in an inert gas or under a flux layer in BeO or MgO crucibles [15]; reaction between nickel and beryllium powders is reported [20] to start at 732°. Table 15 gives the properties of nickel beryllides.

2. Beryllides of Metals of the Platinum Group

Ruthenium beryllides. The existence of $RuBe_2$ has been established [23], but the precise composition and structure of this compound have not been determined. The compound Ru_5Be_{17} has been observed [119] on heating a mixture of ruthenium and beryllium powders in a BeO crucible under argon at 1480°. It was found to be f.c.c. with a = 11.337 Å, and to be isomorphous with the corresponding osmium compound. Its melting point is ≃ 1635°. [122]

Rhodium beryllides. Misch [23] indicated the possibility of the existence of $RhBe_2$ or another compound with Rh : Be = 1 : 2; its X-ray diagram is analogous to that of $IrBe_2$.

Palladium beryllides. Fig. 15 shows the equilibrium diagram of the beryllium–palladium system after Winkler [22]. There is a large number of beryllides in this system: there are five between palladium and the compound PdBe and at least another two between PdBe and beryllium; $PdBe_5$ and $PdBe_{12}$. According to Misch [23], PdBe has the ordered CsCl type of structure with a = = 2.813 kX; these results were confirmed by Belov [123]. $PdBe_5$ has the $MgCu_2$ type f.c.c. structure (like $FeBe_5$ [23,24]) with a = 5.969 Å, [24] pyknometric density 4.56, X-ray density 4.62 g cm^{-3}. $PdBe_5$ does not exhibit superconductivity up to 0.30°K. Yet another phase has been reported [24],

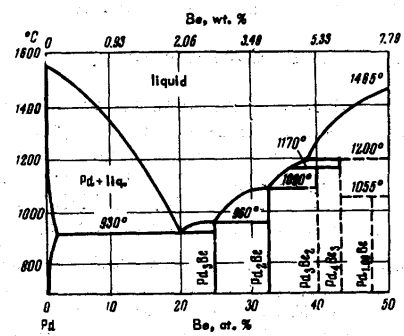

Fig. 15. Part of the equilibrium diagram of the beryllium–palladium system.

$PdBe_{12}$, isomorphous with $MoBe_{12}$, body-centred tetragonal, with a = 7.271 Å, c = 4.251 Å, c/a = 0.585, X-ray density 3.18 g cm^{-3}. The melting points are reported[22] to be: Pd_3Be 960°, Pd_2Be 1090°, Pd_3Be_2 1250°, Pd_4Be_3 1330°, $Pd_{13}Be_{12}$ 1450°, and PdBe 1465°.

Osmium beryllides. According to Misch[23], osmium forms the compound $OsBe_2$ with beryllium.

Iridium beryllides. According to the same author[23], there is the compound $IrBe_2$, the structure of which has not been established,

Platinum beryllides. Platinum and beryllium form the compounds $Pt_{15}Be$ and $PtBe_{12}$. $Pt_{15}Be$ was observed[124] and obtained by reducing a mixture of beryllium oxide and platinum powder at 1150°; it is hexagonal with a = 22.13, c = 27.12 Å. The compound $PtBe_{12}$ has[24] a face-centred tetragonal structure of $MoBe_{12}$ type with a = = 7.237, c = 4.252, c/a = 0.588, X-ray density 4.53 g cm^{-3}. Furthermore, in the same work[24] the possibility of there being a beryllide $PtBe_5$ was mentioned, f.c.c. with a = = 6.004 Å. According to older information[23] there is also a phase Pt_5Be_{21} with the structure of a deformed γ-brass (γ-Ni_5Zn_{21} type). However, the beryllides whose existence has been found most probably and reliably are $Pt_{15}Be$ and $PtBe_{12}$.

G. BERYLLIDES OF THE ACTINIDES

Thorium beryllides. The beryllium–thorium equilibrium diagram, earlier worked out only partially[1] has recently been supplemented considerably[125] (Fig. 16). This system contains the compound $ThBe_{13}$ (92.86 at.% Be) observed earlier by Baenziger and Rundle[40]. Babaeva and Kuznetsova[125] obtained it, like other alloys of the system, by melting 99.3% beryllium with 99.7% thorium in an arc furnace with a tungsten electrode and cooled copper hearth; the atmosphere was chemically pure argon. This compound is f.c.c. ($NaZn_{13}$ type) with a = 10.395 Å[40] (Babaeva and Kuznetsova[125] give a = 10.383 Å). The $ThBe_{13}$ structure has been confirmed[126]. $ThBe_{13}$ melts at ~ 1930°[125] and has good resistance to oxidation in a stream of dry air[79]. The microhardness of $ThBe_{13}$ is[125] ~ 950 kgf × × mm^{-2}. Reaction between compacted beryllium and thorium powders starts at 705°.[20]

Uranium beryllides. The equilibrium diagram of the beryllium–uranium system was developed mainly by Buzzard[127] and Hansen and Anderko's interpretation[16] is shown in Fig. 17. The system includes the compound UBe_{13} with an $NaZn_{13}$ type f.c.c. lattice. Reaction between uranium and beryllium in the form of compacted powders starts at 355°;[20] the compound UBe_{13} can be isolated from uranium-rich alloys by electrolytic dissolution in 10% chromic acid.

However, the main methods of obtaining UBe_{13} are powder metallurgy and vacuum induction melting[128]. In the former, uranium (or uranium hydride UH_3) and beryllium powders are used and the mixtures are sintered at 950–1050° (when beryllium and finely dispersed uranium powders are sintered in pure hydrogen the sintering temperature usually is 1300° and sometimes it reaches 1550°). Vacuum induction melting is done at 1130° (in a quartz container in argon at 1 atm) with subsequent addition of a 10% excess of beryllium (to compensate for the loss of beryllium by vaporisation) and brief homogenisation annealing at 1200–1300°.[128] For the preparation of compact articles of UBe_{13}, the products from sintering or melting are finely ground, pressed in a hydraulic press into blanks of the required shape, which are then sintered in argon at 1550° to give articles with a density > 97%.

Table 16 gives the principal physical properties of uranium beryllide; it must also be added that it exhibits marked brittleness[127]. The microhardness for the "UBe_{12}" phase is reported[59] to be 1300 kgf mm^{-2}.

In chemical respects UBe_{13} reacts with oxygen more slowly than do uranium carbides, nitrides, borides, and metallic uranium itself; it is especially resistant to oxidation at temperatures up to 500°. The oxidation at first follows a linear law and then slowly, by an exponential law, $k = 1.98 \times 10^8 \exp(-26\,200/RT)$ mg cm^{-2} s^{-1}. UBe_{13} behaves similarly with nitrogen, $k = 5.1 \times 10^4 \exp(-25\,800/RT)$, and with water vapour, $k = 5.46 \times 10^4 \exp(-25\,800/RT)$. The change in weight after treatment with water at 100° is 2.2 mg cm^{-2}, in addition to which water brings about rather marked intercrystalline corrosion of uranium beryllide.

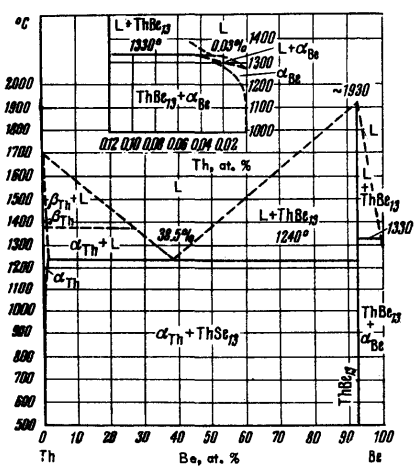

Fig. 16. Equilibrium diagram of the beryllium–thorium system.

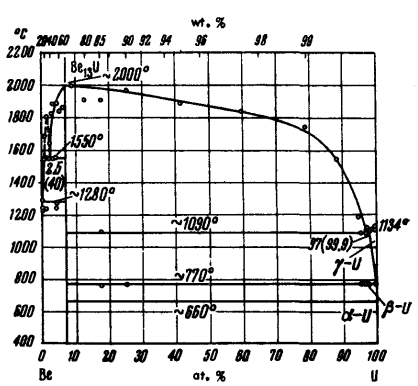

Fig. 17. Equilibrium diagram of the beryllium–uranium system.

TABLE 16. Properties of uranium beryllide.

Property	UBe_{13}
Be content, wt. %	32.9
Structure	f.c.c.
Structural type	$NaZn_{13}$ [40]
Lattice parameter, Å	10.256 [40]
Density, g cm^{-3}	4.373 [40]
Melting point, °C	~2000 [129]
Heat of formation, kcal $mole^{-1}$	37.8 [128]
	39.3 [129]
Thermal conductivity, cal cm^{-1} s^{-1} deg^{-1}	
100°	0.050 [128]
300°	0.058
500°	0.062
650°	0.064
Coefficient of thermal expansion × 10^6 (20°–1000°), deg^{-1}	16.7 [128]
Knoop microhardness, kgf mm^{-2}	
fused	960 [128]
sintered	1155 [128]

Neptunium beryllides. In the reduction of neptunium fluoride by beryllium in a vacuum at 1100–1200°, the compound $NpBe_{13}$ (33.09% Be) was obtained [130]. This is isomorphous with the corresponding phases of thorium and uranium and is f.c.c. ($NaZn_{13}$ type) with a = 10.266 (on the beryllium side) to a = 10.256 Å (on the neptunium side), that is, there is some region of homogeneity. The melting point is above 1400°.

Plutonium beryllides. Plutonium also forms a compound with beryllium of composition $PuBe_{13}$ (32.63% Be) (Fig. 18) [131–133]; it is f.c.c. ($NaZn_{13}$) with a = 10.284 (on the beryllium side) to a = 10.278 Å (on the plutonium side) [130] in the limits of the homogeneity region; according to Konobeevskii [131] a = 10.274 Å. The microhardness of $PuBe_{13}$ [131] is 947 kgf mm^{-2}, the density [131,132] 4.35–4.36 g × × cm^{-3}. The compound is an active source of neutrons [131]. Its m.p. is 1600° and heat of formation 35.7 ± 3.3 kcal × × $mole^{-1}$. [134] $PuBe_{13}$ can be made by melting a mixture of pieces of metallic plutonium and beryllium powder in BeO crucibles under argon in a high-frequency furnace [135].

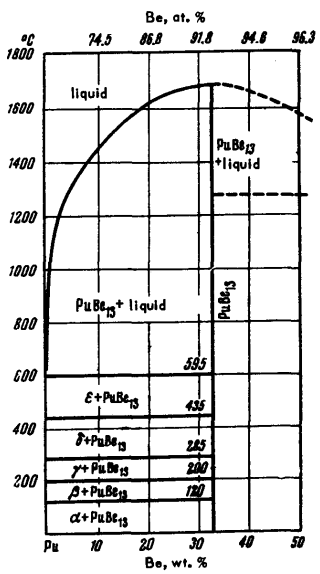

Fig. 18. Part of the equilibrium diagram of the beryllium–plutonium system.

The beryllide $PuBe_{13}$ corresponds to the maximal neutron emission in the Be–Pu system, 67 × 10^6 neutrons × × kg^{-1} s^{-1}. [136]

Americium beryllides. Runnals and Boucher [137] prepared a beryllide, $AmBe_{13}$, by reducing AmF_3 with beryllium in a vacuum (the reaction starts at 900° and proceeds rapidly at 1125°). Like the other beryllides of this composition, it is f.c.c.; a = 10.283 Å (on the beryllium side of the homogeneity region). Its m.p. is 1375°, density 4.376 g cm^{-3} (according to a review [138] 4.35 g cm^{-3}). It has mainly been studied as a source of neutrons [125].

IV. COMPLEX BERYLLIDES

In addition to two-component beryllides, several multicomponent complex beryllides have now been discovered and investigated; they are of considerable scientific and practical interest.

Nowotny and coworkers [88] discovered the ternary beryllides ZrBeSi and HfBeSi, with lattices of the nickel arsenide type ($B8_2$). The compound ZrBeSi has a certain region of homogeneity, within the limits of which the lattice parameters vary from a = 3.722, c = 7.232 Å (at the silicon-rich side) to a = 3.718, c = 7.217 Å (at the beryllium-rich side); for HfBeSi the lattice parameters are equal§: a = 3.693, c = 7.135 Å.

It has been found [139] that there is a continuous series of solid solutions between the compounds $ThBe_{13}$ and UBe_{13} in the Be–Th–U ternary system. An investigation of the physicochemical properties of the solid solution of composition $(Th_{0.9}U_{0.1})Be_{13}$ showed [140] that on oxidation in air at 482° the change in weight of specimens of this alloy is from 0.234 mg cm^{-2} (oxidation time 8 h) to 0.623 mg cm^{-2} (oxidation time 24 h). The physico-technical properties of alloys of (Th, U)Be_{13} with uranium have been described in detail [79].

A ternary compound of the idealised composition AlBeB has been observed [141] in the Al–B–Be system; it is a dark, finely crystalline substance, which crystallises with an antifluorite lattice, the sites of the metal atoms in which are occupied by ordered atoms of Be and Al.

The lattice parameters vary between 4.952 and 4.925 Å, owing to the partial formation by this ternary beryllide of solid solutions with Be_2B.

In the Be–Co–Mn system [142] a ternary phase of composition $MnCo_{0.8}Be_{1.2}$ is found, with the structure of a cubic Laves phase ($MgCu_2$ type) and a = 6.20 Å.

Several complex beryllide phases have been described in reviews [143,144]. In ternary systems with participation of binary beryllides the equilibrium has been described in the systems Be–Fe–P [145] (Fe_2P–$FeBe_2$ and Fe_3P–$FeBe_2$ sections); Be–C–U [146] (UC–Be_2C section); Al–Be–Zr [147] ($ZrBe_9$–Zr_4Al_3, $ZrBe_9$–$ZrAl_2$, $ZrBe_2$–$ZrAl_2$, $ZrBe_{13}$–$ZrAl_{13}$, $ZrBe_{13}$–Al, and $ZrAl_3$–Be sections); Be–Fe–Si [148] (compounds were found: FeSiBe, melting congruently at 1160° and $FeSiBe_3$, melting congruently at 1240°); Be–Cu–Mn [149,150] (Cu–$MnBe_2$); Be–Cu–Ti [150] (Cu–$TiBe_2$ section); Be–Co–Cu [150] (Cu–CoBe section); Cu–$CrBe_2$ [150]; Cu–$FeBe_2$ [150]; Al–Be–Cu [151]; and Be–Cu–Ni [152] (Cu–NiBe section).

§ Presumably on each side of the homogeneity region (Ed. of Translation).

V. STRUCTURE AND PHYSICOCHEMICAL NATURE OF THE BERYLLIDES

Hardly anything has been published about the principles governing the formation of alloys of beryllium and of its compounds with other elements, if one discounts the very general contributions dealing mainly with the possibility of the formation of solid solutions by beryllium [153].

Because the beryllium atom is larger than the boron atom Parthé [154] considers that the beryllides should not be so refractory as the corresponding borides: he thinks that the highest melting points should be expected from the compounds of beryllium with the metals of the sixth period, and bearing in mind the small number of valence electrons of beryllium, with the metals of Groups V and VI, that is, with tantalum and tungsten.

In considering the physicochemical nature of the beryllides it is of prime importance to allow for the peculiar electronic structure of the beryllium atom. The electronic configuration of the beryllium atom is $1s^2 2s^2$; in the formation of crystals, beryllium and compounds are characterised by a single-electron $s \rightarrow p$ promotion [155] with the formation of the electronic configuration $1s^2 2s 2p$. The presence of sp valence electrons brings about the formation of relatively strong covalent bonds between the beryllium atoms, both in the crystal lattice of the metal itself and in the lattices of its compounds with other elements, particularly with metals. In the last instance the tendency of the beryllium atoms to form a covalent bond with one another brings about a statistical diversion to this bond of electrons from the M–Be and M–M bonds, which leads to their corresponding weakening. Corresponding to the formation of a covalent bond between the beryllium atoms, the latter tend to associate in the crystal lattices of the beryllides into more or less intricate structural complexes.

Above all, the peculiarities of the electronic structure of the beryllium atom and its high capability for $s \rightarrow p$ promotion with the formation of a stable sp configuration of the electrons shows in the properties of beryllium itself. As the sp configuration is energetically somewhat more stable than s^2, then on thermal excitation the original $s^2 \rightleftharpoons sp$ equilibrium is shifted to the right and with the prevalence of statistical weight of the sp configuration the crystal structure of the beryllium can be changed, which is also observed in reality [156¶]. The fact that the temperature of this $\alpha \rightarrow \beta$ transformation is close to the melting point of beryllium shows that the sp configuration is not much more stable than the s^2 configuration; this requires a rather high temperature to create the prevailing statistical weight of the sp states and the corresponding modification transformation. Beryllium exhibits the highest heat of fusion among the metals, which is undoubtedly brought about by the presence in it of sp states; this explains the high electronic work function of beryllium, which is not characteristic for ordinary metals with s valence electrons. The tendency of the sp configurations already existing in beryllium to trap electrons and to the formation of the sp^2 and especially sp^3 configurations, which are more stable energetically, brings about both the exceptional tendency of beryllium to contamination by various impurities and the difficulty of removing them, and also the high brittleness of the contaminated beryllium, which in this state contains an electron configuration analogous in energetic state and type to the electron configurations in diamond, silicon, and germanium. The chemical properties of beryllium, which tends, for example, to form compounds of both basic and acidic type, are also evidence of the dual nature of this element, which possesses simultaneously the attributes of a metal (on account of the s electrons) and of a non-metal (on account of the known statistical weight of the sp states).

Just the presence of the sp states, which tend to be stabilised into the states of a higher energetic order sp^2, sp^3, determines the formation by the beryllium atoms of complex elements of structure in compounds, especially with partners, the atoms of which are donors of electrons.

Alkali metal beryllides have the composition MBe_2 ($MgCu_2$ type, characterised by there being in each octant a regular tetrahedron of beryllium atoms, so that their centroids are at the centres of the octants) [157]. Hence the stable tetrahedral configuration of beryllium atoms corresponding to the electronic configuration sp^3 is realised in this structure, for the creation of which the abstraction of electrons from an alkali metal is necessary. In turn the ability of alkali metals to transfer electrons to the Be–Be bond is determined by their ionisation potentials, which decrease from lithium (5.37 eV) to caesium (3.36 eV). Evidently therefore a beryllide has been observed first for potassium [11,158] which has a low ionisation potential (4.32 eV) among those alkali metals whose compounds have been longest and most carefully investigated (Li, Na, K). Possibly, lithium and sodium beryllides either are not formed at all, because of the high ionisation potentials of these metals, or are formed under conditions of strong excitation (high temperatures, strong electrostatic or magnetic fields, electrolysis); on the other hand, the formation of rubidium and caesium beryllides should proceed relatively easily and the fact that it has not yet been observed may be due to the compounds of these rare metals having been insufficiently studied.

On the other hand the possibility of the formation of alkali metal beryllides can be interpreted by assuming that in the formation of metallic crystals from alkali metal atoms s^2 configurations are formed from the valence electrons of the atoms, whereas for the formation of the beryllides the destruction of these configurations is necessary, which is especially easy to complete for the alkali metals starting with potassium owing to the partial promotion of s electrons to the completely vacant d states. Since this promotion increases with the principal quantum number of the d states it is obvious that the most favourable conditions for the formation of a beryllide is with potassium, for which this transition is sharply expressed for the excitation of the s^2 configuration but does not lead to preferential promotion of the s electrons into the d states, owing to the low principal quantum number of the latter; therefore the transfer of some of the s electrons to the beryllium atoms is possible.

The diversion of alkali metal electrons to the Be–Be bond and the formation of covalently bound complexes of beryllium atoms in the beryllide structures should confer on the alkali metal beryllides the character of ionic–covalent compounds with strong asymmetric distribution of the electron density — to sharp displacement of the electrons of the bonds in the direction of the complexes of beryllium atoms. Evidently this asymmetry should increase with a fall in the ionisation potential of the metal

¶ Here, in accordance with the high energetic stability of the sp configuration, the β modification of beryllium based upon it is cubic, whereas the α modification which is based upon the s^2 states is hexagonal, that is, has a lower symmetry.

and with a decrease in the statistical weight of the s^2 configurations; one should expect a parallel reduction in the thermal stability of the beryllides in their disproportionation with formation of groups of beryllium atoms in the vapour state, probably in this instance analogous to the groupings of carbon atoms in the disproportionation of some carbides. It can also be suggested that in these beryllides regions of homogeneity are almost absent or are very narrow.

Beryllides of the metals of the copper subgroup. In the formation of the beryllides of the metals of this subgroup there again appears a tendency for beryllium atoms to form *sp* electronic configurations and corresponding structural elements of beryllium atoms in the lattices of the beryllides; this tendency is combined with the existence of a free s^1 electron of the metal which is comparatively easily transferred to the beryllium atoms. In this connection, copper ($3d^{10}4s^1$, ionisation potential 7.67 eV) readily forms beryllides CuBe, $CuBe_2$, $CuBe_3$ with a growing bridge structure of beryllium atoms in the crystal lattices; in particular, whereas in the structure of CuBe (closely resembling FeSi) the beryllium atoms are isolated, in the $CuBe_2$ structure they form regular tetrahedra situated in the vacancies of the octants of the $MgCu_2$ structure, alternating with magnesium atoms, which are arranged in a diamond-type structure [157]. The greater ease of removal of electrons from the silver atom ($4d^{10}4f^05s^1$, ionisation potential 7.58 eV) facilitates the formation of covalent bonds between the beryllium atoms and shifts the concentration of beryllium in the corresponding beryllides towards higher values $AgBe_2$ and $AgBe_{12}$. Gold forms an even greater number of beryllide phases (Table 1).

In considering the number and nature of the beryllide phases formed by the metals of the copper subgroup, it must be borne in mind that whereas for copper the *s* electrons can be transferred to a partner without the destruction of the stable d^{10} configuration, with silver and gold the completely vacant corresponding *4f* and *5f* states appear, which can bring about partial abstraction of the electrons from the d^{10} configurations with destruction of the latter, and on going from silver to gold the probability of the transfer of the *d* electrons to the *f* states should increase owing to an increase in the energetic stability of the *f* states with rise in the principal quantum number [159]. However, the energetic stability of the d^{10} configuration rises simultaneously and to a greater extent, therefore metallic gold, in particular, has a melting point higher than that of silver, but lower than that of copper, for which (despite the low principal quantum number of the *d* electrons) the *d* electrons are not removed to the *f* states. In connection with the breakdown of the d^{10} configuration of silver and gold the loss of their stability due to the $d \rightarrow f$ transitions creates the possibility of both an increased transfer (compared with copper) of electrons of beryllium to form intricate structural complexes of them with high statistical weight of the sp^3 configurations, and also the possibility of covalent association of the silver or gold atoms with a tendency to the reduction of the destroyed d^{10} states, which brings about for gold the appearance of the lower beryllide phases Au_3Be and Au_2Be†. Analogously, it is to be expected that for silver also lower beryllide phases should be observed.

† On the contrary, in the higher beryllides of the $AuBe_{12}$ type the statistical weight of the d^5 configurations in the gold sublattice is probably very great.

Beryllides of magnesium and the alkaline earth metals. In accordance with the peculiarities of the structure of $NaZn_{13}$ type in which the only beryllium–magnesium compound ($MgBe_{13}$) crystallises, some of the beryllium atoms form icosahedra, the others are at the vertices, the centres of the faces, edges, and in the centre of the cell, and the magnesium atoms are isolated in the centres of the eight cubes into which the cell is divided. Hence in the $MgBe_{13}$ structure the structural motif of the beryllium atoms is particularly strongly expressed.

Beryllium, magnesium, and the alkaline earth metals (calcium, strontium, barium, and radium) have the s^2 configuration of the outer (valency) electrons, which is capable of being converted into the *sp* configuration by $s \rightarrow p$ promotion. As the stability of the *sp* states rises with fall in principal quantum number of the *sp* electrons, the probability of the $s \rightarrow p$ promotion with the formation of these states is much greater, as was shown above for beryllium. For magnesium, owing to the lower stability of the *sp* states the probability of the $s \rightarrow p$ promotion decreases, nevertheless magnesium also retains the feature of a certain dualism of properties, which leads to its separation from the group of alkaline earth metals proper. On passing further to calcium, this gradual fall in non-metallic properties is sharply accelerated with the appearance in calcium of completely vacant *3d* shells into which *s* electrons can be transferred.

Hence the electronic transitions acquire the general form expressed by the scheme $d \rightleftharpoons s^2 \rightleftharpoons sp$. Therefore the lowering of the statistical weight of the *sp* configurations at calcium is due not only to the increase in the principal quantum number of its *sp* electrons, but mainly to $s \rightarrow d$ promotion, which sharply lowers the probability of that of the $s \rightarrow p$. Since the stability of the electron configurations which are converted into the *d* states increases with increase in the principal quantum number of the *d* electrons, then on going from calcium to strontium, barium, and radium the equilibrium $d \rightleftharpoons s^2 \rightleftharpoons sp$ is sharply displaced in the direction of the formation of the configurations of *d* electrons with a diminution in the statistical weight of the *sp* states; the metallic properties of these elements rise correspondingly sharply.

Therefore in the compound $MgBe_{13}$ the "more metallic"‡ magnesium emerges as a donor of *s* electrons and beryllium as an acceptor with the formation of *sp* configurations. The difficulty of making magnesium beryllide described above (see p. 341) is probably explained not only and not so much by the volatility of magnesium and the difficulty of its concentration in the reaction space of the furnace, as by the relative similarity of the electronic structure and energetic states of the beryllium and magnesium, in particular, by the presence in both metals of the difficultly-excited *sp* electronic configurations. In this connection, the calcium beryllide $CaBe_{13}$ is formed much more easily when it is also taken into account that the stable pairs of s^2 electrons are destroyed in consequence of the $s \rightarrow d$ promotion. Therefore $CaBe_{13}$ is also more stable in thermal respects than magnesium beryllide.

It is possible that the absence of such phases for strontium and the other alkaline earth metals is due not only to their having been little investigated, but to the principal considerations that as a result of the $s \rightarrow d$ promotion there is a strong bonding of the electrons and increasing difficulty in their transfer to the beryllium atoms; this

‡ Obviously it would be even better to say "less non-metallic".

difficulty should increase with increase in the principal quantum number of the d electrons, that is, from strontium to radium.

It should be noted that Laube and Nowotny [45] connect the formation of the structural type $NaZn_{13}$ (AB_{13}) with the great difference in the atomic radii r_A and r_B, by showing that this explains the existence of the phases AB_{13} for the beryllides (A = Mg, Ca, Sc, Y, La, Ce, Zr, Hf, Th, U, Pu), zincides (A = Na, Sr, Ba), cadmides (A = K, Rb), and for the same reason such phases are unknown for the magnides, where component B would be magnesium. It is evident that this purely "geometrical" standpoint does not reveal the actual reasons for the formation of beryllide phases of the type AB_{13}.

Beryllides of metals of the zinc subgroup. The increase in the ionisation potentials (up to 9–10.5 eV) compared with the metals previously considered and also the existence of rather stable electronic configurations for the atoms of these metals (type $d^{10}s^2$) greatly hinders the transfer of electrons to beryllium, therefore it is evident that corresponding beryllides have still not been observed, if we rule out the indication of the possibility of the formation of an amalgam $BeHg_2$ on electrolysis, that is, under conditions when there is a rather strong excitation of the mercury atoms (mercury cathode). Under ordinary conditions of heating, the metals of the zinc subgroup are almost inert towards beryllium.

Hence the difficulty or even impossibility of forming beryllides of the metals of the zinc subgroup can most probably be explained by the presence in the crystals of these metals of a high statistical weight of the stable s^2 configurations, which should be destroyed for transfer of some of the s electrons to the beryllium atoms. Such a destruction is mainly possible on account of the $s \rightarrow f$ transitions with cadmium and mercury, which are also realised with sufficiently strong excitation of the atoms of the latter.

Beryllides of the rare-earth metals. It is evident that the picture of the nature of the chemical bond in the rare-earth beryllides is the same in principal as for the beryllides of the alkaline earth metals, owing to the high ionisation potentials (6–7 eV [160]) and the existence of paired outer s electrons for all the lanthanides. In this context, all the r.e.e. beryllides form beryllide phases of the same composition MBe_{13} with $NaZn_{13}$ structure (as do the alkaline earth metal beryllides), but scandium, as a typical d transition metal, forms (in addition to $ScBe_{13}$) also phases of composition Sc_2Be_{17} and $ScBe_5$, which are characteristic of zirconium and hafnium. However, the formation of beryllide phases by the r.e.e. proceeds more easily than that by the alkaline earth metals, apparently owing to the higher energetic position of the $6s^2$ electrons, and also the rather strong screening of the incomplete $4f$ electron shells of the lanthanides. Nevertheless, it must be suggested that their physical properties should differ rather appreciably, owing to a difference in ability to make $f \rightarrow d$ electron transitions and the possibility of the establishment of $5d$ states ($4f^n \rightarrow 4f^{n-1}\,5d^1$) [161,162], the probability of which should rise from gadolinium, on the one hand to lanthanum, and on the other to lutetium. The lattice parameters of the lanthanide beryllides MBe_{13} decrease almost monotonically with rise in atomic number [55] in accordance with the well-known lanthanide contraction. In this the usual breakdown of this monotonicity for europium and ytterbium is essentially not observed, for in the beryllides all the lanthanides behave as formally bivalent metals, and a high statistical weight of stable sp^3 electron configurations of beryllium atoms is formed.

Simultaneously, with increase in the number of electrons in the f shell of the isolated lanthanum atom there is a rise in the statistical weight of the stable f^7 (for elements with seven or less f electrons) or f^{14} (for elements with more than seven f electrons) configurations; correspondingly there should be a drop in the fraction of electrons changing into a delocalised state. Therefore for beryllides with a high statistical weight of f^7 and f^{14} states under the condition of simultaneous localisation of the beryllium valence electrons in stable sp configurations, the appearance of an energy gap and the corresponding semiconducting properties can be expected. The energetic isolation of configurations of electrons localised in the metal and beryllium atoms, with a corresponding decrease in the fraction of non-localised electrons leads to less breakdown of the lattice than would correspond with the relatively high melting points of the lanthanide beryllides, their high hardness, and also ability to disproportionate on melting or vaporisation, as all these features should increase with increase in the statistical weight of the stable f^7 or f^{14} configurations respectively of the atoms of the metal sub-lattice, as is actually observed (Table 2).

It has been noted [55] that the unit-cell volumes of the beryllides MBe_{13} are larger, which is associated with their high beryllium content (92.86 at.%), in which these volumes do not correspond with the rule of the additivity of the metal and beryllium volumes shown by Matyushenko [163] for the beryllides of all simple metals. In other words, since the MBe_{13} beryllides fit the additivity rule for the volumes of the components, then the volume of the beryllium atom should be decreased by ~ 0.23 Å^3 for most beryllides. This can be imagined to be the result of exceptional "close packing" (localisation) of the electrons of the skeletal beryllium atoms associated with the above-mentioned high statistical weight of stable sp electron configurations.

It must be noted that for $ScBe_{13}$ because of the high donor capability of the poorly filled d shell of the scandium atom the formation of the stable electronic configurations of the beryllium atom is accompanied by the appearance of a higher concentration of delocalised electrons, which should involve a lower melting point for this beryllide, more sharply expressed metallic properties, and a lower vapour pressure in thermal dissociation, owing to the greater fraction of electrons passing into the delocalised state and to the more symmetrical distribution of the electron density in the lattice.

Beryllides of the d transition metals. In considering the physicochemical nature and the electronic and crystal structures of the transition metal beryllides with incomplete d electron shells, we must consider the concept of the unimportant difference in distribution of the charge of the d electrons in a metal crystal from that in an isolated atom [164], the possibility of the formation of stable electron configurations of atoms of metals and non-metals [159], the possibility of electron promotion and transfer, and data on the distribution of electrons in the crystals of transition metals into covalently bound and delocalised [165–167]. The scheme of the bonds in the beryllides can be represented in the general form thus:

where M–Be is a predominantly metallic bond, effected by delocalised electrons, the bond Be : Be of predominantly covalent character, and the bond M+M mixed covalent--metallic. Evidently the fraction of the individual types of bonds in metal beryllides depends firstly on the ability of the d shells of these metals to accept or donate electrons with the formation of one or another configuration of localised electrons.

In accordance with ideas about the formation and breaking of stable electronic configurations which have been advanced [159,168,169,176] the stable states formed by the d electrons appear to be d^0, d^5, and d^{10}, the greatest stability being exhibited by the d^5 configuration, and the energetic stability of any configuration of the d electrons increases with increase in the principal quantum number of the d electrons.

For transition metals which possess in the state of isolated atoms the d^1s^2 configuration of valence electrons (scandium and yttrium) and also d^2s^2 (the metals of subgroup IVa) the most probable is the transfer of some of the valency electrons to partners with the formation of a high statistical weight of the d^0 state and a fall in the statistical weight of the d^5 state§. On passing to the metals of Groups V and VI (d^3s^2, d^4s^1, d^4s^2, d^5s^1) with a number of d electrons close to 5, the statistical weight of the d^5 configurations rises and there is a corresponding fall in the donor and rise in the acceptor ability of the atoms, directed to the completion and stabilisation of the d^5 configuration. For the transition metals with more than five electrons in the d shell (Group VIII) the presence of two stable configurations is characteristic: d^5 and d^{10}, the statistical weight of which changes to the benefit of the d^{10} states with rise in the number of electrons in the d shell of the isolated atom.

It must accordingly be expected that the transition metals of Groups III–IV will mainly tend to transfer valency electrons to beryllium atoms with the formation in the metallic sub-lattice of a high statistical weight of the d^0 state, and in the beryllium sub-lattice of covalent groups of beryllium atoms stabilised by valence electrons transferred by the metal atoms. With increase in the relative concentration of beryllium atoms there will be a greater transfer of metal electrons from the valence state in the beryllium atoms which are combined in stable configurations and there is an associated decrease in the concentration of delocalised free electrons, a corresponding decrease in the loosening of the lattice, and a rise in melting point, hardness, and electrical resistivity (Tables 4 and 5). It is noteworthy here that the melting points increase on going from the titanium to the zirconium beryllides, and then decrease for the hafnium beryllides; this is because on going from titanium to hafnium there is a simultaneous change in the stability and the statistical weight of the d^5 configuration and the probability of the promotion of part of the d electron density of zirconium and hafnium to the f state, whereas with zirconium there is evidently a known optimum — with the rise in stability and statistical weight of the d^5 state (leading to a fall is the concentration of the delocalised electrons) for zirconium the process of $d \rightarrow f$ promotion is still not strong enough, leading to a fall in the statistical weight of the d^5 state, to a rise in the weight of the d^0 state with a corresponding increase in the concentration of delocalised electrons, resulting in loosening of the lattice.

Similarly, for the metals of Group V the formation of beryllides should be connected with the breakdown of the electron configuration of beryllium and the transfer of the electrons to the transition metal atoms. However, owing to the tendency of beryllium to form stable electron configurations of type sp^3, it is evident that the same process of transfer of part of the valency electrons from the transition metal atoms to the beryllium occurs, but simultaneously strong covalent bonds are formed between the transition metal atoms [165–167], the more strongly the less they are destroyed by the transfer of electrons to the beryllium atoms. Therefore, for example, for the series of niobium beryllides (Table 6) the melting points of the corresponding phases do not decrease, but rise with increase in the relative proportion of metal, or with decrease in the relative proportion of beryllium. The same also occurs for the tantalum beryllides, and later in Group VI for the beryllides of molybdenum and apparently (judging by hardness)¶ — tungsten. It is interesting that tungsten and rhenium, which have quite stable and not readily excitable d^5 states (formed by d electrons which possess the highest principal quantum numbers, so that in tungsten these states are formed even in the metal crystal: $d^4s^2 \rightarrow d^5s^1$), form phases with the greatest relative amount of beryllium MBe_{22}, which is evidently connected with the considerable ease of transfer to beryllium of their s electrons of the stable d^5 states formed by the localised valence electrons.

For the transition metals having more than five electrons in the d shell of the isolated atom it is possible for both donor and acceptor properties to appear within wide limits, which gives rise to a wide variety of possible combinations of the bond functions and a correspondingly large number of compounds with beryllium, these being formed specially with the platinoids. Here, in those instances when the platinum metal is predominantly a donor, tending to give some of its electrons with a corresponding increase in the statistical weight of the d^5 configuration, phases with a high relative concentration of beryllium are formed predominantly (as for the transition metals of Groups IV–VI), for example, for ruthenium (d^7s^1), osmium (d^6s^2), and iridium (d^7s^2). When the metal is predominately an acceptor, tending to acquire electrons and increase the statistical weight of the d^{10} configurations, then phases with a high relative concentration of metal and a low relative concentration of beryllium are formed, which in this way is prevented from forming covalent groups because the metal atoms do not transfer to it the additional electrons. This occurs, for example, with palladium (d^{10}) and especially with platinum (d^9s^1), for which phases are formed with the lowest beryllium concentrations, right down to Be : M = 1 : 15. Nevertheless these metals, because they retain the probability of forming a type d^5 configuration, also form phases with a high relative concentration of beryllium.

X-Ray crystallographic studies of the beryllides TiBe, $TiBe_2$, Ti_2Be_{17}, and $TiBe_{12}$ have been made and they have

§ Using the results of the X-ray spectroscopic investigation of crystals of transition metals [165–167,177], the statistical weight of the d^5 configurations can be estimated for the metals (%): Sc 18, Y 22, La 23, Ti 43, Zr 52, Hf 55, V 63, Nb 76, Td 81, Cr 73, Mo 88, W 94.

¶ The more so, as hardness in these compounds of metallic type is determined by the concentration of delocalised electrons and by the degree of asymmetry of the electron density distribution, as in metals [170].

been compared with beryllium[66,171]. As a result it was found that for TiBe and $TiBe_2$ [171] the valence electrons of both atoms (titanium and beryllium) are delocalised, which ensures an essentially metallic type of bond with a small contribution from the donor–acceptor interaction of the 3*d* electrons of the titanium with the 2*p* electrons of the beryllium. In Ti_2Be_{17} [66] there is a marked weakening of the degree of overlap of the energy bands of the valence electrons of the components of the alloy and a substantial increase in the role of the interaction between the beryllium atoms, that is, apparently the appearance of strongly covalent Be–Be bonds, which the authors[66] designate as the difference in the "effective electronegativity" of beryllium from the electronegativity of titanium, instead of the practical equality of these quantities of the free atoms and their similar values for the phases containing less beryllium[171]. Hence the results of the X-ray studies of the titanium beryllides confirm well the nature of the change in the type of chemical bond with change in the relative concentration of beryllium atoms in the titanium beryllides.

Unfortunately, there has been no investigation of the superconducting properties of beryllium compounds which would permit several important conclusions about the electronic structure of these compounds to be drawn.

The dependence of the relative change in volume of beryllides of various compositions AB_x on atomic volumes of components A has been investigated[49,55] (Fig. 19). It is evident that the increase in the Be : M ratio leads to a decrease in the fraction of the volume associated with one atom of beryllium, that is, the significant growth in Be : Be covalent bonds and the corresponding packing of the structural complexes of beryllium atoms are again confirmed.

With increase in the Be : M ratio there is a corresponding increase in the coordination number of the M atoms: for the compounds MBe_2 (Laves phase type) the value 16 is characteristic; for the phases MBe_5 ($CaCu_5$ type), M_2Be_{17} (Th_2Zn_{17} type), and MBe_{12} ($ThMn_{12}$ type) 20; for the MBe_{13} phases ($NaZn_{13}$ type) 24. However, the coordination number of M for the MBe_{22} type phases is lower than in

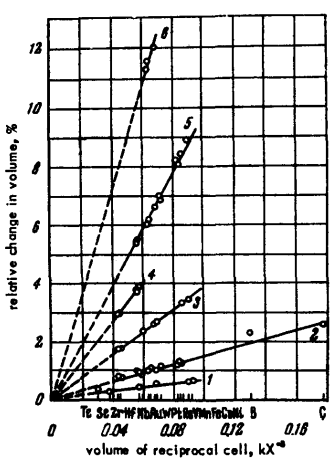

Fig. 19. Dependence of the relative change in the volume of the beryllides ABe_x on the atomic volumes of the components:
1) ABe; 2) ABe_2; 3) ABe_5; 4) $ABe_{8.5}$; 5) ABe_{12}; 6) ABe_{22}.

MBe_{12} and MBe_{13}, which agrees well with the formation here of the most complicated complexes from the beryllium atoms, which are structurally rather strongly isolated from the metal atoms (which in their turn, have a stable state with a high statistical weight of the d^5 configuration).

The electrophysical properties of the transition metal beryllides have hardly been studied at all, but the available data show that the beryllides of metals with a higher statistical weight of d^0 states and a correspondingly high concentration of delocalised electrons have the metallic type of conductivity with a temperature coefficient of resistivity which decreases with fall in the statistical weight of the d^0 state and increase in the weight of the d^5 state. The coefficients of thermal expansion of the beryllides tend to decrease, which is due to the great strength and rigidity of the bonds in their crystal lattices.

Hence the formation of covalent bonds, both between the transition metal atoms and also between the beryllium atoms, on simultaneous transfer of some of the valence electrons of the components into a delocalised state is characteristic of the transition metal beryllides. The transition metal beryllides then can be classified as covalent–metallic compounds with a wide variation in physical and chemical properties within these limits from being present in a predominantly covalent state (at a high statistical weight of stable electronic configurations of the metal and beryllium atoms) to metallic properties, determined by the lower statistical weight of the stable configurations and the large transfer of valence electrons of the components into a delocalised state.

VI. PROMISING FIELDS OF USE OF BERYLLIDES

The high strength of beryllides at high temperatures, especially of transition metal beryllides (Fig. 20), which is about ten times that of ceramics, in conjunction with high oxidation resistance and also high thermal conductivity (which is twice that of high-temperature materials based on oxides) suggests a promising use of beryllides as materials for heat-resistant and other high-temperature alloys with maximal operating temperatures up to 1700°.[172] The industrial use of beryllide heat-resistant materials has been described[80]. Thus, components of space vehicles and guided missiles made from such materials are capable of withstanding a temperature 1.5 times higher than the

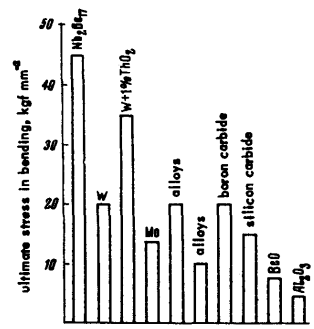

Fig. 20. Comparative strength of the beryllides and other refractory metals (at 1370°).

usual cobalt-, nickel-, and niobium-based alloys. The combination of high strength with low specific gravity (2.7 to 5–6) offers an especially promising use of beryllides in aviation and rocket technology. The resistance of beryllides to thermal shock at low rates of heat transfer and high-temperatures — which are higher than for most metal oxides, but lower than for graphite, fused silicon dioxide, and TiC-based cermets — is important for these fields of use; at high heat transfer rates the beryllides exhibit the same resistance to thermal shock as ThO_2, ZrO_2, and Al_2O_3.

The beryllides are of considerable practical interest for nuclear energy and energetics. Thus the beryllide UBe_{13} is liquid alkali metals is of interest as a nuclear fuel in heat liberating elements of the disperse type [173]. The Be–UBe_{13} dispersion systems have also been described [1,173]. The use of $NbBe_{12}$, YBe_{13}, and $ZrBe_{12}$ as moderators has been discussed [174]. The beryllide $PuBe_{13}$ is used as a neutron source, giving a stable yield of neutrons thanks to the long half-life of plutonium [131].

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The peculiarity of the electronic structure of the beryllium atom, which enables it to form either a metallic bond by means of the valence *s* electrons, or covalent bonds, by means of the *sp* electronic configuration, determines both the dualism of the properties of beryllium itself, which acts simultaneously as a metal and as a non-metal, or as a semi-metal, and also the wide variety of compounds of beryllium with other metals — the beryllides — and their physicochemical properties.

In turn, the variety of properties ensures a wide potential field of use of this important and complex class of chemical compounds, especially in the various branches of high-temperature technology, nuclear physics, semiconductor technology, and in catalysis.

The investigation of the nature of the chemical bond is beryllides is of considerable importance for the development of the principles of contemporary metal chemistry [175] and the creation of new inorganic materials with previously specified physico-technical characteristics.

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THE COLOUR OF DYES AND STERIC HINDRANCE IN THEIR MOLECULES

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Steric hindrance in the molecules of organic dyes has a marked influence on their colour, ability to fluoresce, solubility, and many other physical and chemical properties. The presence of steric hindrance in the molecule quite often makes a dye unsuitable for practical application. With direct dyes the rule exists [1,2] that factors — including steric hindrance — which disturb bond conjugation weaken the affinity of the dye for the fibre, and may result in complete loss of this affinity. Moreover, steric hindrance lowers the intensity of absorption, so that dyes having non-planar molecules yield weaker colours [3]. Steric hindrance in the molecules of cyanine dyes sharply diminishes their ability to sensitise a silver halide emulsion [4]. Thus the problem of steric hindrance in the molecules of organic dyes is of great practical importance.

The chief method for detecting steric hindrance in dye molecules, as in other organic compounds, consists in examining their absorption in the visible or the ultraviolet region of the spectrum.

The absorption spectra of organic compounds depend to a considerable extent on the spatial arrangement of the atoms in their molecules, and sometimes this factor is dominant. The intense and longer-wavelength absorption bands typical of dyes (Burawoy's *K* bands [5]) are associated with $\pi-\pi^*$ electronic transitions, and are caused by the presence in the molecule of an extended system of conjugated double and single bonds, the chromophore [6]. Henceforward we shall confine our discussion to these bands.

Hückel [7] and Pauling [8] showed that the maximum conjugation of multiple bonds is achieved when the molecule has a planar structure, since the axes of the *p* orbitals are then parallel, and the orbitals overlap to the maximum extent. This theoretical conclusion was subsequently confirmed by the X-ray examination of a large number of compounds containing systems of conjugated bonds (*trans*-stilbene, phthalocyanines, cyanine dyes, etc.).

According to the conclusions of quantum-mechanical theory and the results of X-ray structural analysis, the principal structural features of an organic dye molecule are: (1) atoms forming part of the conjugated bond system lie in the same plane; (2) the angles between the bonds involving atoms in the conjugated chain are close to 120°; (3) double bonds in conjugated chains are usually arranged in *trans–trans*-positions; and (4) the lengths of bonds between directly linked atoms in the conjugated chain lie within the range 1.34–1.48 Å (the lengths of bonds between carbon atoms in buta-1,3-diene).

These rules may break down when bulky substituents are present in the conjugated system or adjacent to it. The departures from the normal geometry of the molecule are due to steric hindrance and the mutual repulsion of atoms which are not directly interlinked. If normal angles and a planar structure had been preserved in the molecule, these atoms would have been very close together.

Repulsive forces fall off very rapidly with increase in the interatomic distance. When the latter exceeds the sum of the van der Waals radii, repulsion between the atoms dies away. The van der Waals radii correspond to the minimum distances between atoms in various molecules and molecular crystals, and can be determined from X-ray data.

According to Kitaigorodskii [9] the van der Waals radii of atoms and radicals remain constant to within 0.01 Å on passing from the molecule of one substance to that of another. The van der Waals radii of several atoms and radicals, determined by the above method, are listed in Table 1. [10]

It must be remembered, however, that, as a result of some compression of the electron clouds, atoms can approach, without any considerable consumption of energy, to distances less than the sum of the van der Waals radii. Magat [11] introduced the concept of "effective" radii of atoms and radicals as a limit closer than which atoms could not approach. These effective radii or radii of action depend on the temperature in the sense that the higher the temperature the greater the energy of the colliding atoms, and the more strongly are they deformed on collision.

Although repulsive forces begin to act at distances equal to the sum of the van der Waals radii, the radii of action are in practice more suitable for detecting steric hindrance

TABLE 1.

H 1.20 Å	S 1.85 Å
C 1.80 Å	CH_3 2.00 Å
N 1.50 Å	(C_6H_5) 1.70 Å*
O 1.40 Å	

* Half the thickness of an aromatic ring.

in a molecule. The radii of action of atoms and radicals are known only very roughly. In the case of atoms containing π electrons, they have different values parallel and perpendicular to the plane of the molecule. In view of the difficulty of determining radii of action, somewhat diminished van der Waals radii are often employed[12]. Some workers[13] use the relationship

$$R_{act} = R_{cov} + 0.8 \text{ Å}.$$

The presence or absence of steric hindrance in a planar conjugated molecule is established by drawing the molecule graphically to scale with the normal bond lengths and valency angles. Around each atom or radical is described a circle of radius corresponding to the radius of action. Steric hindrance is then detected from the overlapping of circles belonging to atoms or radicals which are not directly interlinked.

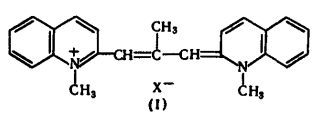
Table 2 gives bond lengths, bond angles, and radii of action for the most important atoms and radicals occurring in dye molecules†.

Fig. 1 shows as example a graphical representation of the cation of 2,2′,9-trimethylcarbocyanine (I).[15] It indicates that a coplanar conformation of this cation is impossible.

More accurate information on steric hindrance is provided by Stuart–Briegleb molecular models[16], which not only enable steric hindrance to be detected in a molecule but also permit the extent of breakdown of molecular coplanarity to be estimated. In these models interatomic

TABLE 2.

Length of bond, Å[13,14]		Radius of action, Å[12]		Angle[12]	
C=C	1.543	H	1.08	C C	
C⋯C (benzene)	1.397	C	1.40	\ / C	125°
C=C	1.353	N	1.35	C C	
C—O	1.43	O	1.26	\ / S	105°
C—N	1.475	S	1.67	C C	
C⋯N (pyridine)	1.37	CH_3	1.80	\ / N	120°
C=N	1.29—1.31	C_2H_5	2.20	C C	
C—S	1.78—1.82			\ / O	105°
C—H	1.007—1.10				



(I)

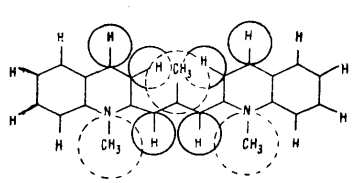
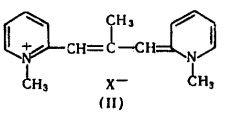


Fig. 1.

† Fuller data on bond lengths and angles in various organic compounds can be found in Wheland's book[14].



(II)

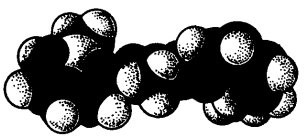
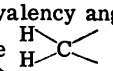
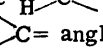


Fig. 2.

distances and angles are strictly fixed, while atoms are incompressible. The only variable parameters are provided by the angles of displacement about bonds. By constructing the model in such a way that atoms are located as close as possible to a single common plane, we can measure or calculate angles of displacement about individual bonds. Fig. 2 illustrates a Stuart–Briegleb model of the dye (II).

From simple geometrical considerations it may be supposed that steric hindrance changes the structure of a molecule in three ways — (1) by the stretching of bonds between atoms, (2) by the distortion of valency angles in a plane, and (3) by displacement about a bond, with one part of the molecule emerging from the plane of the remainder.

Actually, however, bond lengths remain almost unchanged, since the energy required to stretch C–C and C=C bonds is very large (3.25 and 7.05 kcal mole^{-1} respectively to lengthen these bonds by 0.01 Å[17]). Considerably less effort is necessary to distort valency angles in a plane. The energy of deformation of the  angle in the methane molecule and of the  angle in the ethylene molecule by 5.73° (0.1 radian) is respectively 0.39 and 0.26 kcal mole^{-1}.[17] However, displacement about a bond occurs most easily, as about an axis of rotation. The energy of displacement by 0.1 radian about an ethylenic (C=C) and an aromatic (C–C) bond is respectively 0.24 and 0.08 kcal mole^{-1}.[18] For a bond which approximates to a single bond, this energy is close to zero. It follows from these results that the primary effect of steric hindrance will generally be displacement about bonds, which will occur more readily the closer a given bond approximates to a single bond.

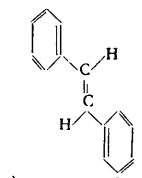
When considering the effect of steric hindrance on the absorption spectrum of a molecule containing a system of conjugated bonds, we must also bear in mind that the stretching of bonds and the distortion of valency angles have relatively little effect on the conjugation of π electrons[19], whereas rotation about a bond reflects the axes of p-electron orbitals from their parallel arrangement. The π-electron interaction energy varies with the square of the cosine of the angle of deflection[20-22]. On rotation through 90°, the atomic p orbitals cease to interact.

Let us now examine the changes in absorption spectrum resulting from steric hindrance and the breakdown of molecular coplanarity in the light-absorbing substance. These changes consist firstly in a displacement in the absorption band, which is usually characterised by the change in wavelength corresponding to maximum absorption (λ_{max}). Secondly a change, usually a decrease, occurs

in the intensity of absorption, which is characterised by the molecular extinction at the absorption maximum (ϵ_{max}).

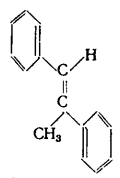
The decrease in absorption intensity is a direct consequence of the diminished mutual overlap of p orbitals in the conjugated system when its coplanarity breaks down. A fall in molecular extinction is therefore the first sign of the appearance of steric hindrance in the absorbing molecule.

The displacement of the absorption band is rather more complicated, since it may occur either towards longer or towards shorter wavelengths. Thus methyl-*trans*-stilbene (IV) absorbs at shorter wavelengths than does *trans*--stilbene (III)[23]:



λ_{max} 294 nm, logϵ 4.44

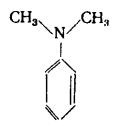
(III)



λ_{max} 272 nm, logϵ 4.30

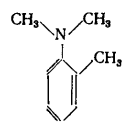
(IV)

NN-Dimethyl-*o*-toluidine (VI) absorbs at shorter wavelengths than does dimethylaniline (V)[24]:



λ_{max} 300 nm, ϵ 13.9 × 10³

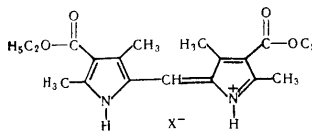
(V)



λ_{max} 277 nm, ϵ 6.0 × 10³

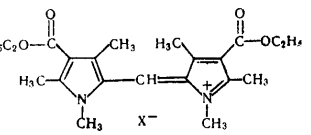
(VI)

In 1942 Brunings and Corwin[25] were the first to show that steric hindrance in the dipyrrylmethene (VIII) produces not a hypsochromic but a bathochromic shift:



λ_{max} 470 nm, ϵ 13.5 × 10⁴

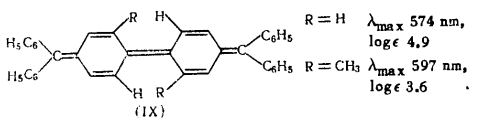
(VII)



λ_{max} 510 nm, ϵ 5.7 × 10⁴

(VIII)

A bathochromic shift has been observed to accompany steric hindrance in Chichibabin's hydrocarbon (IX)[26]:



R = H λ_{max} 574 nm, logϵ 4.9

R = CH₃ λ_{max} 597 nm, logϵ 3.6

(IX)

Absorption of light occurs in the visible and ultraviolet regions when the energy of the quanta of incident light coincide with that of the electronic transitions of the molecule from the ground state to an excited state. The frequency of the adsorbed light is determined by the difference in energy between ground and excited states according to the well--known Bohr formula

$$\nu = \frac{c}{\lambda} = \frac{E' - E_0}{h}.$$

Hence, in order to ascertain how the frequency (or wavelength) absorbed by the molecule changes under the influence of steric hindrance, we must know what changes are produced thereby in the energy of the ground and of the excited states (steric hindrance always increases the energy of a molecule in comparison with one that is free from steric hindrance).

If steric hindrance increases the energy of the excited state more than it does that of the ground state, the molecule will absorb light of higher frequency: i.e. the absorption band will shift to shorter wavelengths, and a hypsochromic shift in the absorption band will be observed. In the opposite case, when steric hindrance increases the energy of the ground state more than that of the excited state, the molecule will absorb light of lower frequency: the absorption band will be displaced to longer wavelengths (bathochromic shift).

Applying the LCAO approximation[27], we determine the order of the mobile (π-electron) bond p'_{rs} as the derivative of the energy E of the π electrons with respect to the exchange integral β_{rs} of the π-electron orbitals of the atoms r and s forming the given bond:

$$p_{rs} = \frac{1}{2}\frac{\partial E}{\partial \beta_{rs}}.$$

As we have seen, the influence of steric hindrance on absorption spectra is due to the disturbance of π-electron conjugation, represented by a decrease in the absolute magnitude of the exchange integral β_{rs}. If the change in the exchange integral is small, the corresponding change in the π-electron energy is[28]:

$$dE = \frac{\partial E}{\partial \beta_{rs}} d\beta_{rs} = 2p_{rs}\, d\beta_{rs}.$$

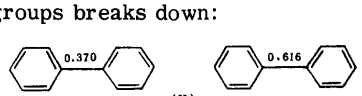
Since excitation involves no change in the relative positions of atoms, the change in exchange integral produced by steric hindrance is the same in ground and excited states. The difference in the change in energy of ground E_0 and excited E' states should depend on the difference in bond order between ground $p_{0,rs}$ and excited p'_{rs} states:

$$d(E' - E_0) = 2d\beta_{rs}(p'_{rs} - p_{0,rs}).$$

The exchange integral is a negative quantity. When it decreases in absolute magnitude, $d\beta_{rs}$ is positive. If, therefore, the bond order is greater in the excited than in the ground state, i.e. if $p'_{rs} - p_{0,rs} > 0$, the energy of the transition $E' - E_0$ increases, since $d(E' - E_0) > 0$, and we should observe a hypsochromic shift. When, on the other hand, $p'_{rs} - p_{0,rs} < 0$ and $d(E' - E_0) < 0$, a bathochromic shift should be observed. In the particular case in which $p'_{rs} - p_{0,rs} = 0$ and $d(E' - E_0) = 0$, steric hindrance does not affect the position of the absorption maximum, although it may influence the fine structure and the intensity of absorption.

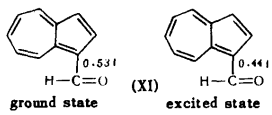
The bond order in the chain of conjugation in a molecule in its ground state can be determined[29] by X-ray examination of its length. Some information can be obtained from infrared and Raman spectra[30]. The experimental determination of bond orders in the excited state of a molecule is difficullt, but some information can be obtained from the vibrational structure of the absorption bands[31].

However, the order of the bonds in which we are interested (only the contribution of the π electrons to the bond order is taken into account), in both ground and excited states, can be calculated to a sufficiently close approximation by quantum-mechanical methods. Calculations by the molecular orbital method are most readily available. They show that the order of the central bond in biphenyl (X) increases on excitation. This is consistent with the observed hypsochromic shift when the coplanarity of the phenyl groups breaks down:

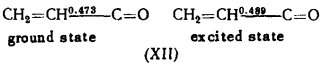


ground state (X) excited state

In just the same way calculation shows, in agreement with experiment, that the order of the bond between the cyclic system and the carbonyl group in azulene-1-aldehyde (XI) is lower in the excited state than in the ground state[28]:

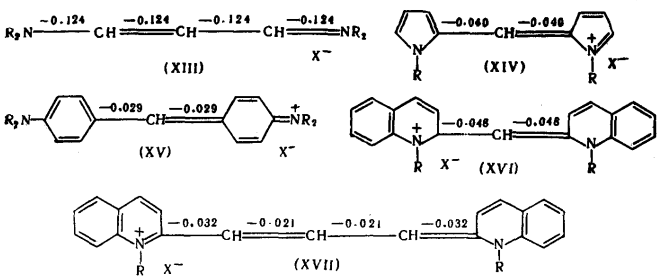


The comparatively small change in order of the similar bond in acryladehyde (XII) explains why no shift in its absorption maximum under the influence of steric hindrance is observed in its derivatives[28]:

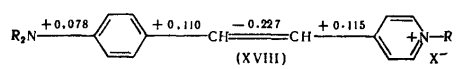


(XII)

Similar calculations (with the usual values for the parameters $\alpha_N = \alpha + \beta$ and $\beta_{CN} = \beta$[32]) show that the excitation of symmetrical polymethine dyes is accompanied by a decrease in order of all bonds in the polymethine chain, for example (with only the differences $p'_{rs} - p_{0,rs}$ indicated)



This rule does not extend to unsymmetrical dyes. For the 4-*p*-dimethylaminostyrylpyridinium cation (XVIII) calculation indicates that excitation will be accompanied by an increase in order of the "single" bonds and a decrease in that of the "double" bond:



Similar calculations have been made for bianthronyl[33], stilbene[34], and nitro-derivatives[35].

Quantum-chemical methods are also useful in enabling general tendencies and regularities to be detected in the changes in bond order accompanying excitation. It has been shown from symmetry considerations, for example, that the order of the central bond in compounds of general formula A–A increases on excitation if this bond is single when the formula is written in the usual way, and decreases if the bond is double or triple (except in the case of cumulenes)[36]. Similar principles have been formulated for the central bonds of symmetrical compounds of general formula Hal–X=Hal$^+$, i.e. for dyes[36].

If we have data on bond orders only in the ground state, we can guess the most probable direction of the change. In fact, if the bond about which deflection occurs is of low order in the ground state, cases in which this bond will have a still lower order should be more rarely met than cases in which it will be of a higher order in the excited state. If, one the other hand, the bond is of high order in the ground state, it is more likely to have a lower order in the excited state. It must be borne in mind here that, on the average, bond orders are lower in an excited state than in the ground state.

This follows from the fact that the energy of a molecule is an additive function of the bond energies, which are proportional to the bond orders. According to the definition of bond order which we have adopted, the coefficient of proportionality between the energy and the order of a bond should be double the exchange integral. Actually, if

$$E' = E_0 + 2\sum_{r<s} p_{rs}\beta_{rs},$$

we have

$$\frac{\partial E}{\partial \beta_{rs}} = 2p_{rs}.$$

The mean decrease in bond order on excitation depends on the transition energy and the number of bonds n involved in the absorption of light. Writing the mean values $\bar{p}$ and $\bar{\beta}$, we obtain

$$2\sum_{r<s} p_{rs}\beta_{rs} = 2n\bar{p}\bar{\beta};\ \bar{p}' - \bar{p}_0 = \frac{E' - E_0}{2n\bar{\beta}}.$$

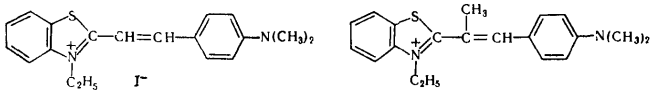
Substituting in this formula $\bar{\beta}$ = 73.2 kcal mole^{-1}[32], the transition energy, and n = 4 for the dye (XIII) (λ_{max} 409 nm), we obtain $\bar{p}' - \bar{p}_0 = -0.119$, in good agreement with the value of -0.124 calculated by the molecular orbital method. It follows from the relationship which has been obtained that the smaller the transition energy and the larger the number of bonds, the smaller is the difference in bond order between ground and excited states. This means that, as the molecule becomes more complicated and the colour of the substance deeper, steric hindrance exerts an ever diminishing effect on the transition energy (the displacement of the absorption band expressed in frequency units decreases). But this does not mean that the shift in the absorption maximum expressed in wavelength units should be smaller, under otherwise similar conditions, in more deeply coloured substances, since the sensitivity of the wavelengths of absorption maxima to changes in transition energy increases rapidly with increase in wavelength. In fact if follows from $\lambda_{max} = \nu_{max}^{-1}$ that $d\lambda_{max} = -\lambda^2_{max} d\nu_{max}$.

The conclusion that bond orders on the average decrease on excitation indicates a tendency of steric hindrance to cause bathochromic shifts. However, deflection about a bond which approaches a single bond in character requires less energy, and occurs first if there is a choice[37]. On the same principle sterically hindered compounds have a smaller energy content and are more stable the lower the order of the bond, rotation about which destroys the conjugation. Therefore we more often meet hypsochromic shifts.

Bond orders in ground and excited states can be estimated also by other quantum-chemical methods, e.g. the valence bond method. With this method it must be borne in mind that the "percentage double-bondedness" is ambiguous owing to a certain arbitrariness in the choice of canonical structures, and bond orders must be determined by Penney's method[38]. The inconvenience associated with this last method, as well as the necessity of taking into account ionic structures for the excited state, complicate application of the valence bond method in comparison with the molecular orbital method. Nevertheless, an empirical approximation of this method, known as the theory of resonance, enables the relative orders of difference bonds in the ground state, or the ratio of the orders of the same bond in ground and excited states, to be determined simply and clearly. The conclusions of this simple method do not usually differ qualitatively from those of the molecular orbital method. Thus the general conclusion that deflection about bonds of low order should result in hypsochromic

shifts, whereas deflection about bonds of high order should result in bathochromic shifts, was first obtained by Wheland [39] on the basis of this particular method.

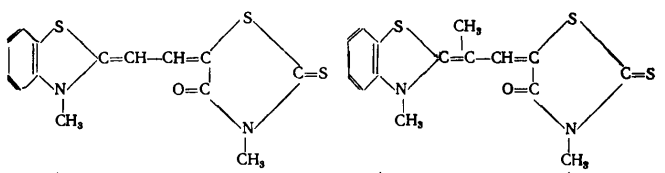
We can illustrate the application of resonance theory by an example [40]: the change from the styryl dye (XIX), having an unsubstituted chain, to its methyl derivative (XX) is accompanied by a diminished intensity of absorption and a marked displacement of the absorption band to shorter wavelengths:



λ_{max} 528 nm, ϵ 11.0×10^4 (XIX)

λ_{max} 481 nm, ϵ 6.2×10^4 (XX)

In the latter dye (XX) steric hindrance arises between the methyl group in the chain and the sulphur atom or the *N*-alkyl group. This interference forces the benzothiazole ring system to be deflected through a certain angle about its bond with the neighbouring carbon atom in the chain as axis, this bond being predominantly single in the ground state. On the other hand, the absorption maximum is displaced to longer wavelengths in merocyanine dyes, e.g. on passing from (XXI), whose chain is unsubstituted, to its methyl derivative (XXII):

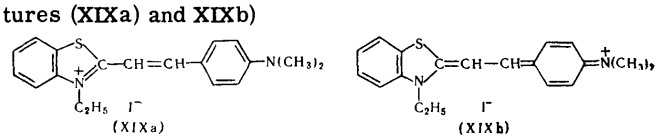


λ_{max} 521 nm, ϵ 9.13×10^4 (XXI)

λ_{max} 542 nm, ϵ 7.75×10^4 (XXII)

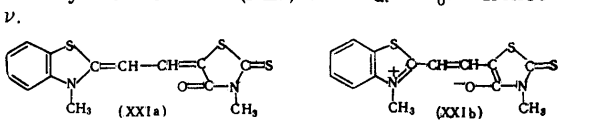
In contrast to (XX), the bond about which the ring system turns in the dye (XXII) in the ground state approximates to a double bond, not a single bond.

The structure of the molecule of (XIX) in both ground and excited states is intermediate between the structures (XIXa) and XIXb)



(XIXa) (XIXb)

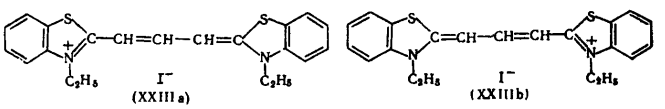
the former predominating in the ground state, and the latter in the excited state. A similar situation is found in the dye (XX). Denoting by E_0 the energy of compound (XIX) in the ground state and by E_0' that of compound (XX), and by E_{ex} and E_{ex}' the energies of these compounds in the excited state, we find that E_0' differs little from E_0, since deflection about a single bond requires no great consumption of energy. But E_{ex}' exceeds E_{ex}, since deflection about a double bond requires a considerable consumption of energy. Consequently the quantum of energy absorbed by the molecule (XX) $h\nu' = E_{ex}' - E_0'$ exceeds that absorbed by the molecule (XIX) $h\nu = E_{ex} - E_0$. Hence $\nu' > \nu$.



(XXIa) (XXIb)

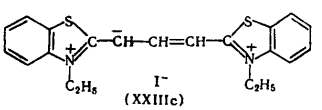
In the case of merocyanines in which a non-polar structure, e.g. (XXIa), predominates in the ground state, whereas a polarised structure (e.g. XXIb), predominates in the excited state, the energy relationships between ground and excited states are the reverse of those above, and $\nu' < \nu$.

In the case of symmetrical polymethine dyes, all carbon–carbon bonds in the polymethine chain have the same length of 1.40–1.41 Å, as has been shown for the thiacarbocyanine (XXIII) [41]



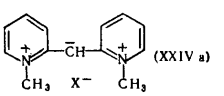
(XXIIIa) (XXIIIb)

The fact that steric hindrance in these dyes produces bathochromic shifts [42] is explained by the theory of resonance in terms of diminished interaction between the limiting structures — (XXIIIa) and (XXIIIb) [43] — resulting from the breakdown of conjugation. The same effect can be explained by a decrease in bond order in the excited state in comparison with the ground state owing to the great weight of bipolar structures of the type (XXIIIc) in the excited state [44].



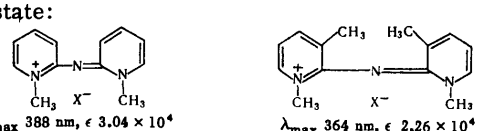
(XXIIIc)

These explanations do not contradict, but on the contrary supplement, one another. It is impossible to say in advance which of the effects should be the more important. This depends on the structure of the given dye. Contrary to Scheibe's original idea [44], it must be remembered that completely symmetrical structures, e.g. (XXIVa)



(XXIV a)

cannot be involved in an incompletely symmetrical excited state [45]. Therefore increase in the weight of such structures, as e.g. in the compounds (XXV) and (XXVI), results in a decrease in bond order not in the excited but in the ground state:



λ_{max} 388 nm, ϵ 3.04×10^4 (XXV)

λ_{max} 364 nm, ϵ 2.26×10^4 (XXVI)

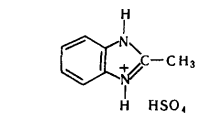
As a consequence, steric hindrance in these compounds produces hypsochromic shifts [46], instead of the bathochromic shifts which are usual for symmetrical dyes.

In the examination of experimental data, it is often difficult to assess the "pure" effect of steric hindrance, especially if it is caused by strong electron-donor or electron-acceptor substituents. In cases of this kind, steric and electronic effects are superposed, and are difficult to separate. In the investigation of steric effects, therefore, they are usually produced by introducing bulky alkyl groups, whose electronic effect is minimal [47].

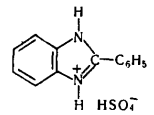
Data known to us on the effect of steric hindrance on the colour of dyes can be separated, to some extent arbitrarily, into two groups. The first group comprises cases in which steric hindrance prevents conjugation of a substituent with the main chromophore of the molecule. The second group consists of cases in which the coplanarity of parts of the chromophore itself is destroyed by steric hindrance.

The effect of steric hindrance on a substituent in a dye molecule is in general fairly simply revealed. The steric hindrance forces the substituent out of coplanarity with the chromophore, and thus diminishes or altogether eliminates

its effect on the absorption of light. An example is provided by replacing the methyl group in the 2-methylbenzimidazolium cation (XXVII) by phenyl, which produces a bathochromic effect[48]:

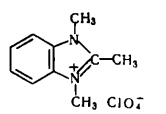


λ_{max} 275 nm, ϵ 0.096 × 10⁴ (XXVII)

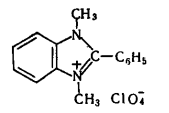


λ_{max} 300 nm, ϵ 2.76 × 10⁴ (XXVIII)

This effect almost disappears if methyl groups are attached to the nitrogen atoms, for they prevent the phenyl from lying in the plane of the heterocycle:

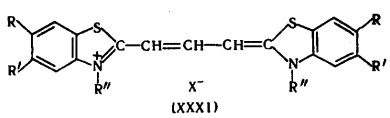


λ_{max} 277 nm, ϵ 0.84 × 10⁴ (XXIX)



λ_{max} 280 nm, ϵ 1.52 × 10⁴ (XXX)

Introduction of a substituent *ortho* to a dialkylamino- or a nitro-group in an aromatic ring produces a hypsochromic displacement of the absorption band owing to steric hindrance[49]. Let us examine in this connection the absorption of thiacarbocyanines of general formula



(XXXI)

which were investigated by Kiprianov and Zhmurova[50]. Comparison of dyes *4* and *1* in Table 3 shows that the introduction of two dimethylamino-groups into the thiacarbocyanine cation considerably deepens the colour and diminishes its intensity (the latter effect being associated with a broadening of the absorption band). If methyl radicals are introduced *ortho* to the dimethylamino-groups (dye *5*), some breakdown occurs in the coplanarity and conjugation of the dimethylamino-groups with the benzene rings, and their influence on the colour is somewhat weakened. In fact we see that the absorption maximum of dye *5* approaches that of dye *2*, and the intensity of absorption increases. The more bulky t-butyl groups force the dimethylamino-groups still further out of the plane of the benzene rings, and practically eliminate their effect on the colour. The narrow and intense absorption band of dye *6* almost coincides with that of dye *3*. In this case steric hindrance has a similar effect to protons binding unshared electron pairs in dimethylamino-groups (dye *7*).

Similar rules were observed by Levkoev et al.[51] on the introduction of halogen atoms *ortho* to dimethylamino--groups in thiacarbocyanines.

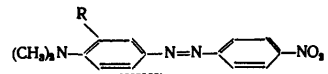
TABLE 3.

Dye No.	R	R′	R″	λ_{max}, nm	$10^{-4}\epsilon$
1	H	H	C_2H_5	558	16.5
2	CH_3	H	C_2H_5	563	14.5
3	$C(CH_3)_3$	H	CH_3	563	14.9
4	H	$N(CH_3)_2$	C_2H_5	608	8.2
5	CH_3	$N(CH_3)_2$	CH_3	575	10.1
6	$C(CH_3)_3$	$N(CH_3)_2$	CH_3	570	14.1
7	H	$\overset{+}{N}H(CH_3)_2$	C_2H_5	558	16.4

TABLE 4.

R	λ_{max}, nm	$10^{-4}\epsilon$
H	475	3.20
CH_3	438	2.20
C_2H_5	425	2.18
iso-C_3H_7	420	1.86

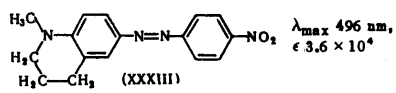
In azo dyes having the structure



(XXXII)

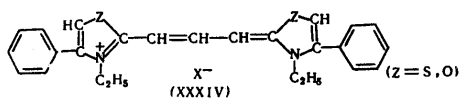
substituents R *ortho* to the dimethylamino-group diminish its auxochromic action and weaken the colour[52] (Table 4).

If the substituent forms a ring with the amino-group, fixing the latter in the plane of the benzene ring (dye XXXIII), it intensifies instead of weakening the colour:



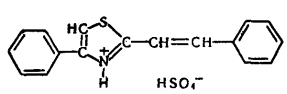
λ_{max} 496 nm, ϵ 3.6 × 10⁴ (XXXIII)

Aryl radicals in the 4,4′-positions of the cations of thiazolo- and oxazolo-cyanines have little effect on the absorption of light by these dyes, whereas the same aryls in the 5,5′-positions greatly deepen the colour[53–55]. It was suggested that, as a result of steric hindrance, aryl groups in the 4,4′-positions are not coplanar with the thiazole or oxazole rings:

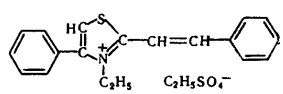


(XXXIV)

This hypothesis could be confirmed[56] by comparing the absorption curves of the sulphate (XXXV) and the ethyl sulphate (XXXVI) of 4-phenyl-2-styrylthiazoles:



λ_{max} 358 nm, ϵ 2.4 × 10⁴ (XXXV)



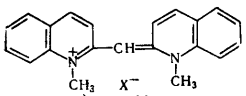
λ_{max} 355 nm, ϵ 1.82 × 10⁴ (XXXVI)

Steric hindrance was practically absent in the cation of the sulphate, and the phenyl group produced a bathochromic displacement of the absorption maximum.

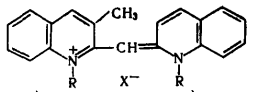
Experimental data on the effect of steric hindrance in the chromophores of dyes are far more varied. Cyanine dyes form the most convenient subject for investigations of this type. In them the length of the conjugated chain can be altered comparatively easily, as can substituents differing in bulk and electronic character be introduced into it, and hydrogen atoms substituted in the heterocyclic rings. Displacements of maxima resulting from the appearance of steric hindrance can be very conveniently observed in cyanine dyes, with their narrow and intense absorption bands.

The first systematic investigation in this field was undertaken by Scheibe[57]. He found that introduction of a methyl group into position 3 of the pseudocyanine dye (XXXVII), with the formation of (XXXVIII), produces no shift in the absorption maximum if methyl groups are

attached to the nitrogen atoms. Replacement of these methyl by ethyl groups produces a bathochromic shift:

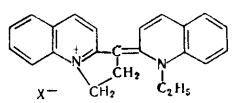


λ_{max} 522 nm
(XXXVII)

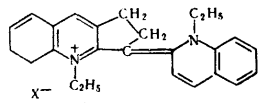


R = CH_3 λ_{max} 523 R = C_2H_5 λ_{max} 535 nm
(XXXVIII)

The substantial change in the absorption maximum on passing from methyl to ethyl groups attached to the nitrogen atoms in itself shows that steric hindrance is involved here. Passing from (XXXVII) to the dyes (XXXIX) and (XL) will give an increase in steric hindrance and a sharp increase in the bathochromic shift:

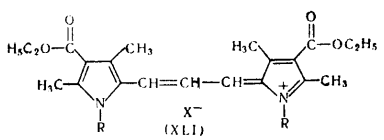


λ_{max} 575 nm
(XXXIX)



λ_{max} 583 nm
(XL)

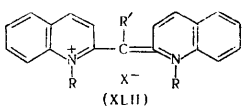
Brooker et al.[43] showed that the previously mentioned Brunings–Corwin effect was associated with a loss of coplanarity, not with the electronic character of the methyl group. In the vinylogue (XLI) of dipyrrylmethane, replacement by methyl groups of the hydrogen atoms attached to the nitrogen atoms produces merely a slight hypsochromic shift, since the coplanarity of the molecule is not thereby disturbed:



(XLI)

R = H λ_{max} 595 nm
R = CH_3 λ_{max} 581 nm

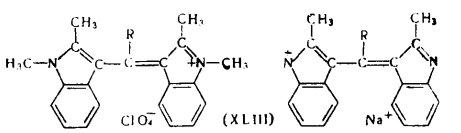
Brooker found an effect, similar to that described for dyes (XXXVII) and (XXXVIII), on introducing an alkyl radical into the methine group of pseudocyanines:



(XLII)

R	R′	λ_{max} nm
CH_3	H	520
CH_3	CH_3	574.5
C_2H_5	H	522.5
C_2H_5	C_2H_5	584

Similar facts had been observed even before Brooker's work. They had either remained unnoticed, as occurred, for example, with the indocyanines

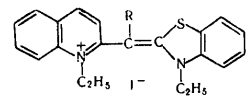


(XLIII)

R = H λ_{max} 482 nm
R = C_6H_5 λ_{max} 518 nm

R = H λ_{max} 482 nm
R = C_6H_5 λ_{max} 526 nm

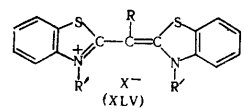
synthesised by König[58] in 1925, or were puzzling. Thus Götze[59] in 1936 was the first to prepare *meso*-methylthia--2-quinocyanine (XLIV, R = CH_3), but he thought that he was dealing with a more complicated substance, since its violet colour differed sharply from the orange colour of the unsubstituted dye‡:



R = H λ_{max} 486 nm; R = CH_3 λ_{max} 545 nm[60]
(XLIV)

Bathochromic shifts accompanying the introduction of bulky alkyl substituents into the methine groups of monomethinecyanines were observed by Kiprianov and Ushenko[42] and by Fry and Kendall[62] in thiacyanines, by Jeffreys and Knott[63] in pyrrolocyanines, and by Hamer[60] in unsymmetrical cyanines.

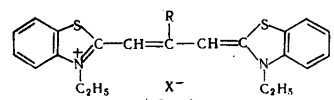
Kiprianov et al.[64] showed that this effect is actually associated with steric hindrance. Studying the monomethinecyanines (XLV), they found that replacement of the methine hydrogen atom by a methyl group produces no steric hindrance if hydrogen atoms are attached to the nitrogen atoms. Such replacement results in a loss of coplanarity and a bathochromic shift only when alkyl groups are attached to the nitrogen atoms:



(XLV)

R	R′	λ_{max} nm
H	H	425
CH_3	H	425
H	CH_3	425
CH_3	CH_3	465

A *meso*-methyl group does not give rise to steric hindrance in the thiacarbocyanines (XLVI, R = CH_3)[4]. The slight hypsochromic shift without appreciable decrease in intensity is explained by its electronic effect[65]. In the dye (XLVI, R = C_6H_5) the phenyl group, because of steric hindrance, lies in a plane perpendicular to the rest of the molecule. Conjugation of the phenyl group with the chromophore of the dye disappears, and the group has no significant effect on the colour[66]:



(XLVI)

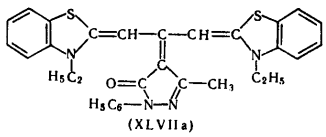
R = H λ_{max} 558 nm, R = CH_3 λ_{max} 543 nm,[67] R = C_6H_5 λ_{max} 560 nm

Even the introduction of polar substituents — $N(CH_3)_2$, OH, O^- — into the *para* position of this phenyl group does not significantly affect the absorption maximum[68].

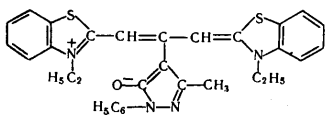
Brooker observed an interesting phenomenon, which he termed allopolar isomerism[69], in some trinuclear dyes. The dye (XLVII) can be represented by three limiting structures, a non-polar form (XLVIIa) and two bipolar

‡ The non-planar structure of this dye was confirmed in 1960 by X-ray examination, the angle between the planes of the quinoline and the benzothiazole rings being 60°.[61]

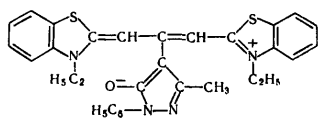
structures — (XLVIIb) and (XLVIIc) — having the same energy:



(XLVIIa)



(XLVIIb)

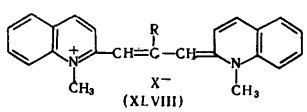


(XLVIIc)

As can be seen from Fig. 3, it is not possible for all three ring systems in the dye (XLVII) to lie in the same plane: at least one of them must be perpendicular to the other two.

In a polar solvent (methanol) this dye gives an absorption curve (Fig. 4*B*) which is typical of thiacarbocyanines. Hence the molecule is polarised in methanolic solution, the two benzothiazole systems lying in one plane, while the pyrazolone ring, with a negative charge on the carbonyl oxygen atom, is deflected from this plane as a result of rotation about the single bond, as in structures (XLVIIb) and (XLVIIc) (Fig. 3*B*). In a non-polar solvent (lutidine) the absorption curve (Fig. 4*C*) is quite different in shape, resembling that of a merocyanine based on a benzothiazole and a pyrazolone ring. It is obvious that in lutidine solution the benzothiazole and pyrazolone systems lie in the same plane, while the second benzothiazole ring system is deflected out of this plane — structures (XLVIIa) and (XLVIIb) (Fig. 3*C*).

Introduction of a methyl group into the *meso* position of the 2,2′-carbocyanine (XLVIII) now causes steric hindrance[70], which is eliminated by deflection of the quinoline rings about the bonds of the polymethine chain. The consequence is a bathochromic shift:



(XLVIII)

R = H λ_{max} 607 nm,[71]
R = CH_3 λ_{max} 649 nm,[7]
R = C_6H_5 λ_{max} 648 nm,[71]

In the dye (XLVIII) with R = C_6H_5 the phenyl group lies in a plane perpendicular to that of the chromophore, but even in this position it, like the methyl group, causes steric hindrance.

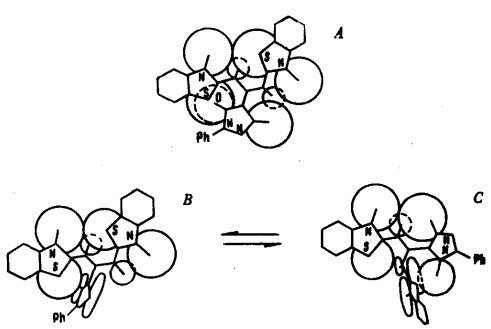


Fig. 3.

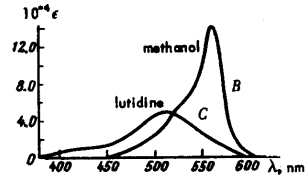
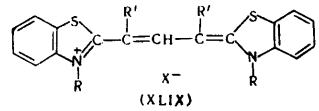


Fig. 4.

Kiprianov and his coworkers have shown that alkyl or aryl groups in the $\alpha\gamma$ positions of the polymethine chain of thiacarbocyanines (XLIX) cause steric hindrance[42,72]:

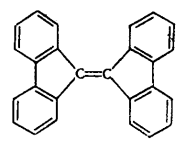


(XLIX)

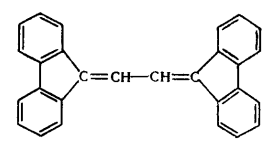
R	R′	λ_{max} nm
CH_3	H	559
CH_3	CH_3	577
CH_3	C_2H_5	571
CH_3	iso-C_3H_7	576
CH_3	C_6H_5	580
C_6H_5	H	565
C_6H_5	CH_3	602

Deflection of the benzothiazole ring systems about the bonds of the polymethine chain results in a bathochromic shift, which is especially marked if phenyl radicals are attached to the nitrogen atoms.

An interesting case occurs when steric hindrance present in a lower vinylogue because of the large volume of the ring systems of the dye disappears when the polymethine chain is lengthened. For example, 9,9′-bifluorenylidene (L) is more deeply coloured than is its vinylogue (LI)[73]. In the non-coplanar dye (L) the ring systems have been deflected about a bond which approximates to a double bond. This has led to a bathochromic shift in the absorption maximum exceeding the vinylene shift in the maximum on passing from (L) to (LI).

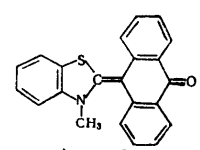


λ_{max} 458 nm
(L)

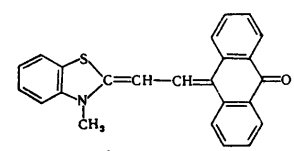


λ_{max} 444 nm
(LI)

A similar phenomenon is observed in the quinone methides (LII) and (LIII)[74].

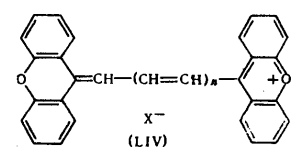


λ_{max} 551 nm
(LII)



λ_{max} 537 nm
(LIII)

In xanthocyanine (LIV, n = 0) the bathochromic shift due to breakdown of coplanarity is detected from the decrease in the vinylene shift on passing from n = 0 to n = 1:[75]

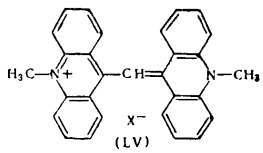


(LIV)

		$\Delta\lambda_{max}$
n = 0	λ_{max} 648 nm	
		57 nm
n = 1	λ_{max} 705 nm	
		80 nm
n = 2	λ_{max} 785 nm	
		80 nm
n = 3	λ_{max} 865 nm	

The considerable breakdown in coplanarity in acridinomethinecyanine (LV) is detected from the very low extinction

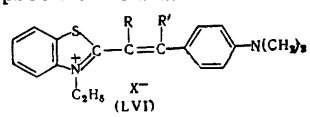
of this dye and the wide absorption band without any distinct maximum[43]:



(LV)

In dyes having a high degree of electronic asymmetry the effect of steric hindrance will depend on the order of the bond about which the ring systems of the dye have been deflected.

In styryls (LVI) with substituents in the β or α position, deflection of the benzothiazole and benzene ring systems occurs about bonds of diminished order, resulting in a hypsochromic shift[76]:

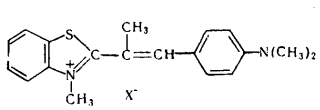


(LVI)

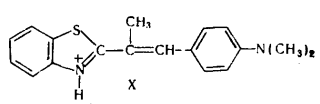
R=H R′=H λ_{max} 530 nm
R=CH_3 R′=H λ_{max} 481 nm
R=H R′=CH_3 λ_{max} 518 nm

Similar results were obtained by Brooker[43] and by Hamer[60].

The presence of steric hindrance in the styryl dye (LVII) has been confirmed by Kiprianov and Tolmachev, who showed that its analogue (LVIII), in which steric hindrance should not be present, absorbs at considerably longer wavelengths[77]:

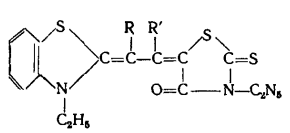


λ_{max} 478 nm
(LVII)



λ_{max} 496 nm
(LVIII)

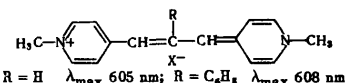
The bonds between the heterocyclic systems and the neighbouring methine groups in merocyanines (LIX) are of high order, and deflection of the rings about these bonds results in bathochromic shifts[78]:



(LIX)

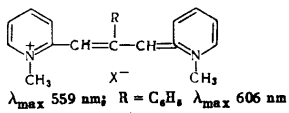
R	R′	λ_{max} nm
H	H	524
CH_3	H	540
C_6H_5	H	536
H	CH_3	532
H	C_6H_5	542

Kiprianov and Dyadusha[15] made a spectroscopic study of steric hindrance in symmetrical and unsymmetrical *meso*-phenylcarbocyanines. They showed that in the 4,4′-pyridocarbocyanines (LX) a *meso*-phenyl group produces no change in the absorption maximum, as in the case of the thiacarbocyanines discussed earlier:



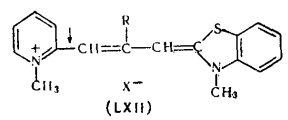
R = H λ_{max} 605 nm; R = C_6H_5 λ_{max} 608 nm
(LX)

A phenyl group in the same position in 2,2′-pyridocarbocyanines (LXI) results in appreciable steric hindrance, as in the dye (XLVIII, R = C_6H_5). Deflection of the rings about bonds in the polymethine chain produces a bathochromic shift:



R = H λ_{max} 559 nm; R = C_6H_5 λ_{max} 606 nm
(LXI)

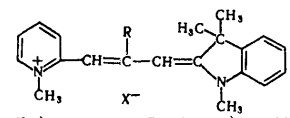
In unsymmetrical dyes (LXII) bonds of higher and lower order alternate in the chain. The degree of non-equivalence of the bonds is measured by the deviation[79,80] (the displacement, towards shorter wavelengths, of the absorption maximum of the unsymmetrical dye from the arithmetic mean of the absorption maxima of the corresponding symmetrical dyes):



(LXII)

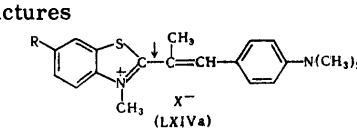
R=H λ_{max} 536 nm
deviation 22.5 nm
R=C_6H_5 λ_{max} 544 nm
deviation 39 nm

In the dye (LXII) with R = C_6H_5 steric hindrance between the pyridine ring and the phenyl group is removed by rotation about a bond (shown by the arrow in the formula) of rather diminished order. This results in a smaller bathochromic shift on passing from the dye (LXII) with R = H to the corresponding dye with R = C_6H_5 compared with the similar bathochromic shift in the dye (LXI). Deflection of the pyridine ring about a bond of diminished order results in a still greater decrease in the order of this bond, and hence in an increase in the deviation. With a sufficiently large difference in basic character between the ring systems, as e.g. in the dye (LXIII), the bathochromic shift is replaced by a hypsochromic shift:

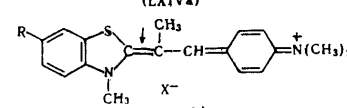


R = H λ_{max} 509 nm; R = C_6H_5 λ_{max} 460 nm
(LXIII)

Kiprianov and Mikhailenko have investigated, on polymethine dyes of several types, how displacement of the absorption maximum changes with variation in the order of the bond about which the ring systems of the dye are deflected. In styryl dyes (LXIV)[40] the first of the two limiting structures



(LXIVa)



(LXIVb)

predominates in the ground state, and deflection of the benzothiazole ring system caused by interference with the methyl group takes place about a bond which approaches a single bond in character. The consequence of this is a hypsochromic shift in the absorption maximum on passing from the dye with an unsubstituted chain to its methyl derivative. However, the order of this bond — marked by an arrow in formula (LXIVa) — can be to some extent varied by introducing various polar substituents into the benzothiazole system. The electron-donor dimethylamino-group, where R = $N(CH_3)_2$, by increasing the basic strength of the benzothiazole moiety still further stabilises structure (LXIVa), lowers the order of the bond shown by the arrow, and increases the hypsochromic displacement of the maximum to 80 nm. The electron-acceptor nitro-group (R = NO_2) will give the opposite effect (hypsochromic shift decreases to 50 nm) (Table 5).

In the unsymmetrical carbocyanine (LXV) having an unsubstituted chain (R = R′ = H) the cationic charge is located predominantly on the more basic ring system (with the dimethylamino-group in position 6), and the bond ***a*** is

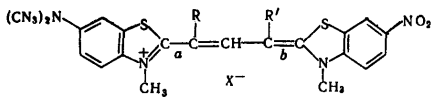
TABLE 5.

R	$\Delta\lambda_{max}(H \rightarrow CH_3)$, nm
$N(CH_3)_2$	80
H	61
NO_2	50

TABLE 6.

Solvent	$\Delta\lambda_{max}(H \rightarrow CH_3)$, nm	Solvent	$\Delta\lambda_{max}(H \rightarrow CH_3)$, nm
Water	—65	Acetone	+ 4
Methanol	—57	Chloroform	+12

closer to a single bond, while bond *b* is closer to a double bond (deviation 15 nm)[81]:

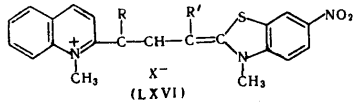


R=H R′=H λ_{max} 586 nm, deviation 15 nm,
R=CH_3 R′=H λ_{max} 556 nm, deviation 44.5 nm,
R=H R′=CH_3 λ_{max} 601 nm, deviation 7 nm.

(LXV)

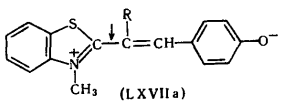
Replacement by methyl of the methine hydrogen adjacent to the bond *a* — dye (**LXV**) with R = CH_3 and R′ = H — shifts the absorption maximum to shorter wavelengths, whereas similar substitution in the methine group adjacent to bond *b* (R = H and R′ = CH_3) displaces the absorption maximum to longer wavelengths, compared with the dye having an unsubstituted chain, although the steric hindrance is the same in the two dyes. In dye (**LXV**) with R = CH_3 and R′ = H, as also in dye (LXII) with R = C_6H_5, deflection of the left-hand benzothiazole system about a bond of lower order increases the deviation to 44.5 nm. Deflection of the right-hand ring system about bond *b* in dye (**LXV**) with R = H and R′ = CH_3 lowers the order of this bond. The electronic asymmetry of the dye is diminished, as is evident from the decrease in the deviation to 7 nm.

Similar phenomena are observed in unsymmetrical carbocyanines (LXVI) made up of quinoline ring system (the more basic) and a 6-nitrobenzothiazole system (the less basic).

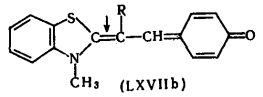


(LXVI)

In the zwitterionic anhydro-bases of the *p*-hydroxystyrenes



(LXVIIa)



(LXVIIb)

the order of individual bonds in the conjugated chain can be varied as desired by dissolving the dye in solvents of different polarities. This is the explanation of the solvatochromism of zwitterionic dyes[82]. The bond marked by the arrow in formulae (LXVIIa) and (LXVIIb) is closer to a single bond in polar solvents, and closer to a double bond in non-polar solvents. In conformity with this, substitution of methyl for hydrogen as the radical R in the dye (LXVII) will give different displacements of the absorption maximum depending on the solvent, as can be seen from Table 6.[74]

If the zwitterionic dyes — (LXVII), R = H and R = CH_3 — are dissolved not in pure solvents but in mixtures of the weakly polar pyridine and the strongly polar water, smooth curves are obtained showing how the displacement (H → CH_3) in the absorption maximum varies

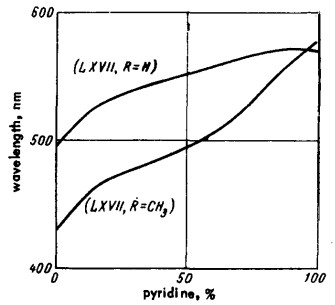
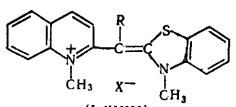


Fig. 5.

with the percentage of pyridine in the water. It is seen from Fig. 5 that, as the pyridine content increases (the polarity decreases), the colour of the anhydro-bases deepens, the order of the bond marked by an arrow increases, and the curve of the dye with R = CH_3 approaches the curve for the anhydro-base having an unsubstituted chain (the hypsochromic shift decreases). With a mixture containing 90% of pyridine, the bonds in the chromophore of the anhydro-base level out (the colour being the deepest), and in this region the hypsochromic shift changes to a bathochromic shift.

Bulky polar substituents may have two effects — steric and electronic — and it is often difficult to determine the proportion of each. The introduction of phenyl and *p*-nitrophenyl radicals into the methine group of a monomethinecyanine (**LXVIII**, R = H) causes a bathochromic shift. These radicals undoubtedly lie in a plane perpendicular to that of the heterocyclic ring systems, and the observed bathochromic shifts are due, as in the case of the methyl group, solely to steric effects[60]:

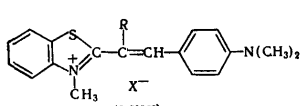


(LXVIII)

R	λ_{max} nm
H	486
CH_3	545
C_6H_5	552
p-$C_6H_4NO_2$	548
$COOC_2H_5$	474

When, however, the hydrogen atom is substituted by an ethoxycarbonyl group, a hypsochromic instead of a bathochromic shift is observed, owing to the predominating electronic effect of the ethoxycarbonyl group. It is known that negative substituents in the α position of a chain should give a hypsochromic displacement of the absorption band[83,84].

In the styryls (**LXIX**), the two effects act in the same direction, which explains the comparatively large hypsochromic shift when R = $COOC_2H_5$:

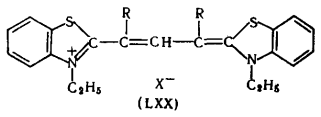


(LXIX)

R=H λ_{max} 525 nm
R=CH_3 λ_{max} 460 nm
R=$COOC_2H_5$ λ_{max} 418 nm

The effect of polar substituents in the *meso* position of thiacarbocyanines is determined solely by the electronic effect: electron-donor substituents produce a hypsochromic shift[85], whereas electron-acceptor substituents produce a bathochromic shift[86,87].

Alkoxy- and aroxy-groups in the $\alpha\gamma$ positions of the thiacarbocyanine (LXX) cause a bathochromic shift[72,88,89], the magnitude of which is little affected by the nature of the aryl:

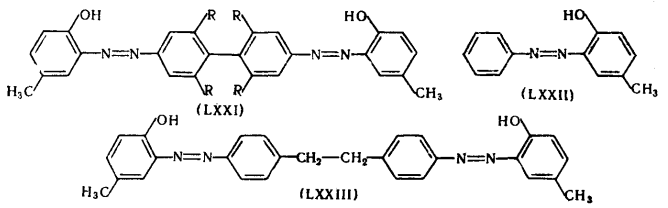


(LXX)

R	λ_{max}, nm
H	558
OCH_3	586
OC_6H_5	589
p-OC_6H_4Cl	585
p-$OC_6H_4OCH_3$	590
OH	565

The slight decrease in intensity compared with the dye having an unsubstituted chain and the fact that the dye with $R = C_6H_5$ is a good sensitiser[4] indicate that the electronic effect predominates in this case.

The effect of steric hindrance on the colour of dyes of other classes has been far less studied than in the case of polymethine dyes.



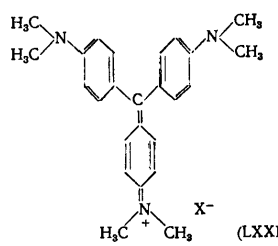
(LXXI)

(LXXII)

(LXXIII)

Brode and his coworkers[90,91] studied the effect of steric hindrance in bisazo dyes which are derivatives of biphenyl. They found that the absorption curve of the dye (LXXI) with $R = CH_3$ resembles that of the dyes (LXXII) and (LXXIII): i.e. there is no conjugation between the biphenyl rings in the first of these three dyes. Similar results have been reported in a series of papers by Krasovitskii[92].

Di- and tri-arylmethane dyes having a symmetrical distribution of the electron cloud resemble symmetrical polymethine dyes. In Crystal Violet



(LXXIV)

only the nitrogen and the central carbon atom lie in the same plane, owing to steric interference (of the *ortho*-hydrogen atoms). The benzene rings have been turned relative to one another in such a way that the structure of the dye resembles a three-bladed propeller. Calculation shows that each benzene ring should turn through 18°.[93]

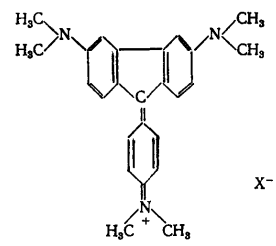
The introduction of methyl groups *ortho* to the central carbon atom results in further deflection of the rings about bonds of enhanced order, which leads to an increase in the bathochromic shift (Table 7)[94]. The uniform displacement of the absorption maximum with increasing number of *o*-methyl groups suggests that all three rings have been deflected to the same extent (in the 2,2′,2″-trimethyl derivative the angle of deflection should be about 34°). But the 2,6-dimethyl derivative gives a larger shift per methyl group. It is possible that in this case the xylidine

TABLE 7.

Methylated Crystal Violets	λ_{max}, nm	Methylated Crystal Violets	λ_{max}, nm
Crystal Violet (LXXIV)	589	2,2′,2″-Trimethyl	614
2-Methyl	597	2,6-Dimethyl	614.5
2,2″-Dimethyl	605		

ring has been greatly rotated, and the charge is concentrated on the two dimethylaniline rings, as in Malachite Green. Similar results have been obtained for Michler's Hydrol Blue.

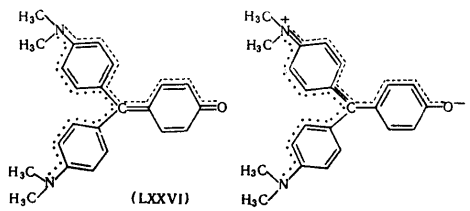
Barker[95] fixed two rings of Crystal Violet in a plane by means of an additional valency bond, but obtained an unexpected result: the dye (LXXV) proved to be more deeply coloured than Crystal Violet. This result was subsequently explained by formation of the new C–C bond and the greater possibility of conjugation of the rings[96,97].



(LXXV)

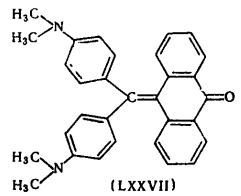
X^- λ_{max} 647 nm

A phenomenon analogous to Brooker's allopolar isomerism was observed by Hünig[98] in sterically hindered triphenylmethane dyes. Of the two possible systems of conjugation in tetramethyldiaminofuchsone (LXXVI) — the dimethylaminofuchsone system (broken line in the formula) and the Malachite Green system (dotted line in the formula) — only the former is developed. The dye has one absorption maximum, which migrates with change in the polarity of the solvent:

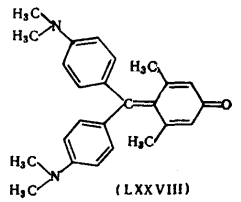


(LXXVI)

In the dyes (LXXVII) and (LXXVIII), which exhibit great steric hindrance, the quinone ring is turned relative to the rest of the molecule, and partly emerges from conjugation:



(LXXVII)

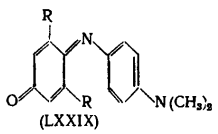


(LXXVIII)

The spectra of these dyes now reveal two systems of conjugation (the dyes each have two absorption maxima, one of which migrates with change in the polarity of the medium). When acid is added to solutions of the dyes, only the absorption maximum remains which does not vary with

change in the solvent, and this undoubtedly belongs to the conjugation system of Malachite Green.

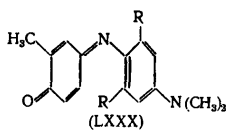
In the indaniline dye (LXXIX, R = H) the C⁄N\C angle is less than 180°, and a value of 120° has been assumed[99] by analogy with *cis*-azobenzene:



(LXXIX)

R = H λ_{max} 634 nm
R = CH_3 λ_{max} 653 nm

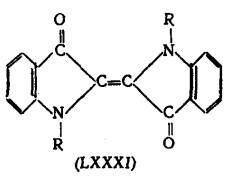
Steric hindrance in the dye (LXXIX, R = CH_3) between one of the *o*-methyl groups and the dimethylaniline ring is eliminated only by turning the quinone ring about the double bond, which causes a bathochromic shift. Rotation of the dimethylaniline ring about the single bond does not eliminate steric hindrance, which remains between one of the methyl groups and the plane of the benzene ring of the dimethylaniline[100]. In the dye (LXXX, R = CH_3), on the other hand, the dimethylaniline ring turns about a bond which is close to a single bond, with a hypsochromic shift as a consequence[101]:



(LXXX)

R = H λ_{max} 630 nm
R = CH_3 λ_{max} 610 nm

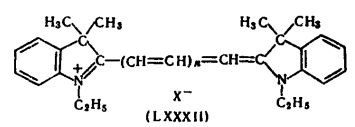
Although the order of the central bond in indigo (0.628)[102] is less than that of an aromatic bond (0.667), it should decrease on excitation, as has been shown by Dyadyusha[36]. This explains the bathochromic shift on passing from indigo (LXXXI, R = H) to dimethylindigo (LXXXI, R = CH_3), in which Weinstein and Wyman assume the presence of steric hindrance[103]:



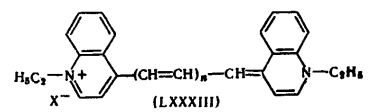
(LXXXI)

R = H λ_{max} 591 nm
R = CH_3 λ_{max} 644.5 nm

Hofer et al.[12] showed that steric hindrance inhibits the fluorescence of cyanine dyes. Indocyanines (LXXXII) and 4-quinocyanines (LXXXIII) fluoresce only when $n = 2$ or above. This observation was confirmed by Kiprianov and Ushenko[104], who also observed that sterically hindered dyes show practically no fluorescence.

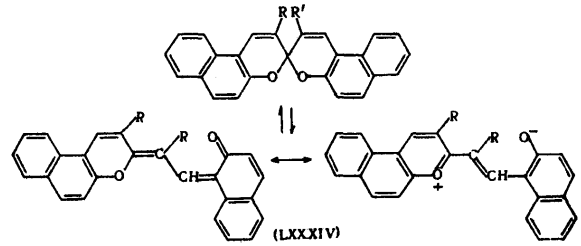


(LXXXII)



(LXXXIII)

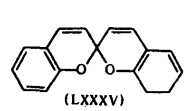
Finally, the effect of steric hindrance on the thermochromism of spiropyrans (LXXXIV), which has been studied by Koelsch[105], must be noted. The thermochromism of colourless spiropyrans (LXXXIV, R = H) is due to their conversion with ring-opening into a coloured form:



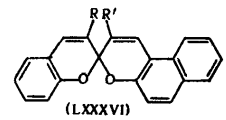
(LXXXIV)

In the spiropyran (LXXXIV) with R = CH_3, the form with opened rings exhibits greater steric hindrance than the spiro-form, in which the rings are mutually perpendicular: therefore ring-opening does not occur, and thermochromism is not observed.

Dibenzospiropyran (LXXXV) is non-thermochromic, since conversion into the form with open rings involves the formation of an unstable *o*-benzoquinone ring. Benzonaphthospiropyran (LXXXVI, R = R′ = H) exhibits thermochromism, probably with the formation of a naphthaquinone ring.



(LXXXV)



(LXXXVI)

In this connection, the difference between the spiropyrans (LXXXVI, R = CH_3 and R′ = H) and (LXXXVI, R = H and R′ = CH_3) is interesting. The former is thermochromic, since formation of the modification with open rings occurs without strain. The latter compound does not exhibit thermochromism, since formation of the modification with open rings involves steric hindrance.

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THE MECHANISM OF HALOGENATION OF ALKENES WITH A QUATERNARY CARBON ATOM AT THE DOUBLE BOND

I. V. Bodrikov and Z. S. Smolyan

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I. INTRODUCTION

Millions of tons of various halogen derivatives of hydrocarbons are produced every year over the whole world and used in many branches of industry, agriculture, and everyday life [1].

This review deals with information on the mechanism of the very interesting reactions that occur in the halogenation of unsaturated hydrocarbons with a quaternary carbon atom at the double bond (with 2-methylpropene as a particular example). Up to now there have been different views on the mechanism of these reactions, and we kept this in mind in compiling the review.

It seemed that a critical analysis of the available publications together with a presentation of experimental results obtained by the authors of the review would bring a certain amount of clarity to this problem.

II. EARLY VIEWS ON THE MECHANISM OF ANOMALOUS CHLORINATION

In 1884 Sheshukov found that when chlorine acts on 2-methylpropene, instead of the expected saturated dichloro-derivatives, the main products of the reaction were monochlorides of the allyl and vinyl types [2].

Later L'vov and his students showed [3-8] that trimethylethylene [2-methylbut-2-ene], tetramethylethylene [2,3-dimethylbut-2-ene], and unsymmetrical ethylmethylethylene [pent-2-ene] also react with chlorine in an unusual manner. Subsequently, reactions of this type, which were termed anomalous, were the object of thorough study.

A number of schemes were proposed to explain the formation of allyl and vinyl monochlorides, and also saturated dichlorides, when alkenes are chlorinated.

L'vov and coworkers considered that chlorination reactions of unsaturated hydrocarbons proceed through two successive steps [9-11]:

$$C_nH_{2n} + Cl_2 \rightarrow C_nH_{2n}Cl_2;$$
$$C_nH_{2n}Cl_2 \rightarrow C_nH_{2n-1}Cl + HCl.$$

It was supposed that an unstable dichloride is first formed, which decomposes into hydrogen chloride and an unsaturated monochloride with displacement of the double bond.

This view has been shown to be untenable by thermodynamic [12] and kinetic [13] results on the decomposition of dichlorides, and also by a comparison of the results of dehydrochlorination of saturated dichlorides with unbranched and branched hydrocarbon skeletons.

It is well known that the low-temperature chlorination of ethylene leads to the formation of dichloroethane, and only an insignificant amount of vinyl chloride is obtained as a by-product [14-16]. Under comparable conditions the reaction of chlorine with 2-methylpropene gives mainly unsaturated monochlorides, although the dichlorides of both alkenes are about equally stable.

As one of us has shown [12], the dehydrochlorination of 1,2-dichloroethane with a conversion of 80% is achieved at 400° when the reaction is initiated with molecular chlorine (1%). In the absence of initiators, the analogous conversion of 1,2-dichloroethane into vinyl chloride requires a temperature of 480–500°. [17] According to Striegler [18], 1,2-dichloro-2-methylpropane is also dehydrochlorinated at 500° with 77.5% conversion into 2-methylallyl chloride and dimethylvinyl chloride, which are present in the reaction mixture in the constant ratio of 75 : 25. Moreover, Tishchenko [19] checked the doubtful results of Pauly and Lieck [20], who only obtained an addition product at the carbon–carbon double bond by the action of chlorine on mesityl oxide, and found that when one mole of chlorine acts on two moles of 2-methylpent-2-en-4-one, 60–70% of 3-chloro-2-methylpent-1-en-4-one is obtained. The 2,3-dichloro-2-methylpentan-4-one obtained together with the unsaturated monochloride in this reaction decomposes by the Wagner–Saytzeff rule with liberation of hydrogen chloride to form a mixture of 3-chloro-2-methylpent-1-en-4-one and 3-chloro-2-methylpent-2-en-4-one.

The scheme proposed by Ostromyslenskii [21] for the chlorination of alkenes with a quaternary carbon atom at the double bond has not brought clarity into this field and has the same disadvantages as L'vov's scheme. By the action of chlorine on 2-methylbut-2-ene, the author obtained almost equal amounts of t-pentyl chloride and the unsaturated chloromethylbutene, and explained this by the elimination of a molecule of hydrogen chloride from the saturated dichloride produced. The liberated hydrogen chloride then combines with 2-methylbut-2-ene to give a saturated monochloride, that is, it is assumed that there is an unusual transfer of the elements of hydrogen chloride from the dichloride molecule to the ethylene bond of the initial alkene:

$$C_5H_{10} + Cl_2 \rightarrow C_5H_{10}Cl_2;$$
$$C_5H_{10}Cl_2 + C_5H_{10} \rightarrow C_5H_9Cl + C_5H_{11}Cl.$$

III. HOMOLYTIC MECHANISM OF CHLORINATION

For a long time due attention was not given in world literature to the work of Russian chemists mentioned above, and it was only in the 40's that these investigations

were continued. Deanesly [22] found that the addition of chlorine to alkenes is initiated by the reaction in which hydrogen is replaced by chlorine in alkanes present at the same time. Since that time, American workers have continued the study of the chlorination of alkenes with the object of preparing unsaturated chloro-derivatives [23-27].

Solodar' and Markin [28] have analysed the work of this school (see also Refs. 29 and 30). Furthermore, Smolyan and coworkers [31] have reviewed the mechanism of substituting chlorination, dealing with examples of the halogenation of saturated hydrocarbons under different conditions (initiated, photochemical, thermal, etc.).

American workers who studied the high-temperature and low-temperature chlorination of alkenes used a radical scheme for chlorination by substitution. Thus, Burgin and coworkers [32] proposed a scheme for the chlorination of 2-methylpropene at low temperatures according to which 2-methylallyl chloride is formed by the migration of a hydrogen atom from one of the methyl groups. The formation of unsaturated monochlorides in the non-photochemical chlorination of ethylene [15,16,33,34] at room temperature, and of pent-2-ene [35] in carbon tetrachloride solution was also explained by the direct replacement of hydrogen. Stewart and Weidenbaum attempted to associate a three-atom chlorine molecule with the formation of unsaturated monohalo-derivatives [36]. They suggested that in chlorination, a chlorine radical formed by thermal chain generation reacts by two competing routes.

$$Cl^{\cdot} + Cl_2 \rightarrow Cl_3,$$
$$\text{or } Cl^{\cdot} + C_2H_4 \rightarrow C_2H_4Cl.$$

It was assumed that the active three-atom chlorine molecule reacts preferentially by the addition route.

Groll and Hearne [24], who studied the reaction of alkenes with chlorine at different temperatures, showed that there are certain critical temperatures above which monochlorides are formed preferentially:

	°C
2-Methylpropene	< -40
Pent-2-ene	125 — 200
But-2-ene	150 — 225
Propene	200 — 350
Ethylene	250 — 350

This temperature "threshold" was found to be lowest for hydrocarbons with a quaternary carbon atom at the double bond. A "threshold" was not established for 2-methylpropene, and this caused the authors to have doubts about the existence of a critical temperature for this hydrocarbon. Only recently, Lishnevskii and Sergeev succeeded in obtaining the addition product (1,2-dichloro-2-methylpropane) in 87% yield by the reaction of frozen layers of 2-methylpropene with chlorine [37]. It was also previously reported [38] that when chlorine is passed through a mixture of pentenes cooled to -17°, the reaction proceeds without the formation of hydrogen chloride, but a slight increase in temperature promoted elimination of the latter. The proportions of the reagents, as well as the temperature, affect the direction of the reaction. A deficiency of chlorine in the reaction zone increases the yield of unsaturated monochlorides [27]. For example, in the chlorination of butenes at 380–390°, the optimal ratio of alkene to chlorine is 3.5 : 1, [39] and for 2-methylpropene the ratio is 1.5–2.0 : 1. [18] The mechanism of substituting chlorination proposed by American workers cannot explain why unsaturated monochlorides of the allyl type are formed and why chlorine does not replace hydrogen in all possible positions.

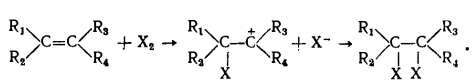
The active state postulated by Hass [40] for hydrogen atoms linked with carbon atoms in the α-position to the double bond also does not explain these contradictions. Indeed, in substituting chlorination, the probability of replacement of hydrogen by chlorine is the same for any position [41-43].

The formation of unsaturated monochloro-derivatives in high-temperature halogenation may occur partly by L'vov's scheme. Thus, a study of the chlorination of ethylene in a reactor with a moving heat carrier at 400–500° showed that vinyl chloride is partly formed through 1,2-dichloroethane with subsequent dehydrochlorination [44]. Moreover, as Reeve and coworkers have shown [45,46], in the gas-phase chlorination of 2-methylpropene containing the tracer carbon isotope ^{14}C (2-methyl-[1-^{14}C]prop-1-ene) at 0°, it is the extreme carbon atom linked to the double bond that is chlorinated, and not the methyl groups. The formation of unsaturated monochloro-derivatives in the low-temperature chlorination of alkenes is accompanied by the displacement of the double bond; according to Azinger, this indicates a heterolytic halogenation process at low temperatures [47]. On the other hand, it is highly probable that the high-temperature chlorination of alkenes in the absence of a thin film [48] proceeds by a homolytic mechanism [49,50]. A proof of this is the reduction of the temperature of gas-phase chlorination in the presence of additives that promote the formation of free radicals [25]. Semenov [51], who examined two competing radical reactions in the chlorination of ethylene — substitution and addition of chlorine with reference to energy factors — established a relation between the rate of substitution and the temperature of the process.

It should be mentioned that the main defect in the interpretation by American workers of the mechanism of chlorination of alkenes with a quaternary atom at the double bond is the unfounded extension of the principles of high-temperature and initiated halogenation to low-temperature chlorination under non-photochemical conditions.

IV. HETEROLYTIC MECHANISM OF HALOGENATION

The action of chlorine on alkenes with a quaternary carbon atom at the double bond is dealt with in greatest detail in the papers of Tishchenko and coworkers [52-56]. A heterolytic mechanism proposed for the halogenation of straight-chain alkenes was used to interpret the experimental results. Francis [57] studied the halogenation of ethylene in dilute aqueous solutions of various salts and observed the formation of mixed addition compounds. The reaction of bromine with ethylene in solutions of sodium chloride or nitrate gives 2-bromo-1-chloroethane or 2-bromoethyl nitrate respectively as the main product; with iodine in sodium chloride solution the main product is 1-chloro-2-iodoethane. The author explained the production of mixed products by the intermediate formation of a carbonium ion of the type $[R-\underset{|}{C}Br-\underset{|}{C}R]^{+}$ in the bromination. Ingold [58] and Robinson [59] proposed the following scheme for the mechanism of halogenation of alkenes:



The authors consider that this reaction is electrophilic; the molecule taking part in the addition is first polarised,

and this is followed by attack on the substrate by the positive halide ion, which leads to the formation of an organic cation. The halide anion reacts with the latter to give the final addition product. Ingold used the addition of iodine monochloride to propene to illustrate this scheme [60]. The distribution of electron density in the ICl molecule corresponds [61] to the formula I^+-Cl^-; on the other hand, the electron density of the π bond of propene is displaced because of the positive inductive effect of the CH_3-group [62] (from a calculation of the limiting electron density for divinyl and isoprene molecules carried out by Hayashi), which permits the scheme for this reaction to be represented as follows:

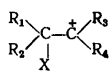
$$H_3C\rightarrow CH=\overset{\delta-}{C}H_2 + Cl-I^+ \longrightarrow CH_3-\overset{+}{C}H-CH_2I + Cl^- \longrightarrow CH_3-CHCl-CH_2I.$$

This mechanism is similar to that proposed by Nenitzescu for the iodination of alkenes [63].

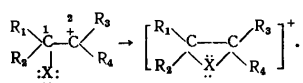
Other workers have also pointed out that an organic cation is formed in the first stage of the reaction of molecular halogens with the ethylene bond [64,65].

Moreover, the existence of various carbonium ions is confirmed by numerous investigations in which NMR spectra [66], ultraviolet spectra [67-74], cryoscopy [75-77], and chemical methods [76,78-80] have been used.

However, the question of the structure of the carbonium ion is still debatable [81]. Thus, it has been noted that the structure of the organic ion proposed by Ingold and Robinson is not in accord with the stereospecificity of the addition [82]. In the hypothetical ion



free rotation is possible round the single C–C bond, which should lead to the formation of *cis*- and *trans*-adducts in equal amounts. Nevertheless, *trans*-products are mainly formed in a number of instances [83]. Since a halogen atom with an unshared pair of electrons in *p*-orbitals is close to the positively charged carbon atom in the intermediate carbonium ion, Roberts and Kimball have suggested that interaction leading to the formation of a bond is possible between the centre of the carbonium ion and halogen atoms [84]. The structure of the intermediate carbonium ion would then be close to a three-membered ring:



The preparation of stable cyclic onium compounds in the aromatic series has confirmed this hypothesis [65].

An analysis of published results made by Bethell and Gold [81] is also in favour of the cyclic cation of Roberts and Kimball.

We shall see below that this hypothesis provides a fairly good interpretation of addition to a multiple bond, although it is subject to the criticism that considerable bond strain is required for the formation of a three-membered ring [86].

However, the formation of *cis*- and *trans*-adducts in additions, at least to the ethylene bond, cannot be unambiguously related to the structure of the intermediate complex.

It is well known that the internal rotation of groups of molecules relative to one another has several potential energy minima for a complete rotation round a single bond. It has been shown by various physical methods that for molecules of the general formulae XH_2C-CH_2X and XH_2C-CH_2Y (X and Y = Cl, Br, I, CH_3, OH, etc.) the *trans*-configuration is the most stable [87-89].

Less stable forms, which have been found together with the *trans*-isomer in a study of the liquid and gaseous states of 1,2-dihaloethanes, are gauche conformations, obtained from the *trans*-form by rotation of one of the CH_2X-groups of the molecule through an angle of $\pm 120°$. [90,91]

The *cis*-form of the rotational isomers is the least stable of known conformations [91]. The stability of *trans*-isomers may be the main reason for the preferential formation of *trans*-adducts in the addition of halogens to alkenes.

Later a new interpretation was put forward for the structure of the intermediate addition complex, which Dewar termed a π complex [92,93]. With both aromatic compounds [94-96] and unsaturated aliphatic compounds [97], the formation of complexes by halogen molecules, which are electron donors, is due to the presence of low antibonding orbitals in iodine, bromine, and chlorine molecules [98] and their considerable polarisability [96]. Freed and Sancier [97] studied the spectra of frozen solutions of iodine in alkenes and their solutions in propane at temperatures from -196° to -43°; the authors assumed that cooling to a low temperature would reduce the rate of addition of halogen to alkenes and increase the concentration of pre-reaction complexes. This assumption was recently confirmed by a thermographic investigation of the propene–bromine system, in which it was shown by the use of low temperatures and special freezing-out procedures that the complex-formation and final-product stages could be separated, and the intermediate complex could be accumulated [99]. In propane, iodine gives only a visible band at 520 nm, with no bands right down to 210 nm. The addition of propene displaces the visible band and produces an intense band with a maximum at 280 nm, similar to that observed in aromatic complexes.

Analysis of published data [100,101] indicates that the new ultraviolet absorption band is due to a complex formed by donor–acceptor interaction between halogen molecules and unsaturated compounds, which is also called a charge-transfer complex [101].

The heats of formation of complexes of iodine with aromatic compounds are estimated at 1 kcal $mole^{-1}$. [102] For alkenes this value is somewhat less than 1 kcal $mole^{-1}$, with the exception of the 2-methylpropene complex, the heat of formation of which is somewhat higher [100].

In spite of such low intermolecular bond energies in associations of halogens with unsaturated hydrocarbons, a review of published information shows that these are not associations of a purely cohesion type. This is indicated by the results of a thermographic investigation of the propene–bromine system [99], evaluation of which showed that the heat of formation of the propene–bromine complex is not less than 5 kcal $mole^{-1}$.

A study [96] of the infrared absorption spectra of the cyclohexene–iodine system showed a reduction in the vibrational frequency of the C=C bond from 1650 to 1524 cm^{-1}, which was considered to be due to the formation of a cyclohexene–iodine π complex.

A reduction of the vibrational frequency of chlorine dissolved in benzene and its derivatives has also been observed; the reduction in frequency increases with increasing electron density in the ring.

According to Mulliken [98,103], the most probable structure for the complex is that in which the halogen molecule is symmetrically arranged in a plane parallel to the benzene ring, because this ensures maximum overlap of selected orbitals [98,103].

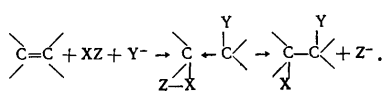
If the molecule of alkene or aromatic compound is unsymmetrical, then the electron density of the bond between the donor and acceptor in the π complex does not have a plane of symmetry perpendicular to the C–C bond. The positively charged halogen atom in such a π complex is situated closest to the carbon atom with the highest electron density [104].

Terenin [100], developing the intermolecular-complex hypothesis, concluded that in the formation of the complex its components are partially ionised, for example, $C_6^{+\delta}H_6.I_2^{-\delta}$, that is, part of the charge is transferred to the iodine molecule, which becomes negatively charged.

Later it was shown [101] that the degree of electron transfer from the donor to the acceptor may vary from zero to complete transfer; in the latter instance, neutral molecules are converted into ion-radicals.

According to Reutov [104], in the course of chemical reaction the π complex can assume the structure of Roberts and Kimball's carbonium ion [84].

Shilov and coworkers [86,105-110] showed that the π complex hypothesis is in good agreement with the kinetics of heterolytic addition reactions; in particular, it explains the emergence of termolecular kinetic equations. If the reaction is of the ionic type, a termolecular addition mechanism operates:



The molecule XZ behaves as an electron acceptor and Y^- behaves as a donor.

Shilov called this a termolecular acceptor–donor mechanism [106]. In the general case a termolecular heterolytic mechanism leads to a termolecular kinetic equation

$$v = k[A][XZ][Y^-],$$

where [A] is the concentration of unsaturated compound. This form of kinetic equation has been established for many addition reactions [111-113].

It is assumed that in electrophilic addition the unsaturated molecule A forms a complex with the electron acceptor XZ in the equilibrium state (constant R), which then reacts with the donor Y^- (nucleophilic reagent).

The reaction rate is then given by the equation

$$v = RC_{AXZ}C_Y = RkC_AC_{XZ}C_Y.$$

A number of reactions are also known in which halogenation of unsaturated hydrocarbons in solvents with a certain polarity, particularly acetic acid, is a second-order reaction [114-118]:

$$v = k[A][Hal_2].$$

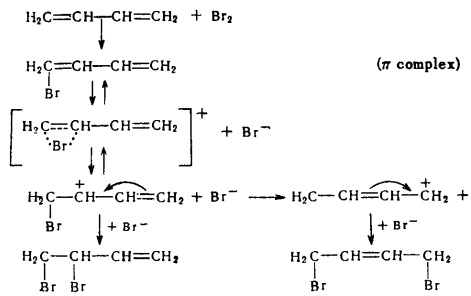
However, the addition of bromine to alkenes in solvents that are no more polar than acetic acid, or in acetic acid over a certain concentration range (0.025 M), is third-order [119-122]:

$$v = k[A][Hal_2]^2.$$

Dilution, increase in temperature, or addition of water reduces the order of reaction from third to second.

The results of these kinetic investigations show that the agent attacking the double bond is a halogen molecule, which acts on alkenes as an electrophilic reagent [123].

Petrov adduces sufficiently convincing facts in favour of the two-stage mechanism for electrophilic 1,2- and 1,4--addition to 1,3-diene compounds [124]. He considers the π complex to be the first combination with the diene; this complex is then converted into a carbonium ion:



The idea of association of the halogen with the π bond of the alkene, and of the charge-transfer complex [100,101], and the results of a thermographic study [99] are in agreement with this scheme.

In explaining the mechanism of chlorination of alkenes with a quaternary carbon atom at the double bond, Tishchenko [52-56] considered that the process is initiated by the addition of the positive end of the halogen molecule, as in all electrophilic additions to the carbon atom with the maximal electron density. The polarisation of the multiple bond in asymmetrical disubstituted and trisubstituted ethylenes is achieved by the positive inductive effect of alkyl groups [62,125].

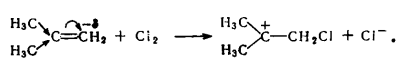
Because of the displacement of four electron pairs to the double bond, symmetrical tetrasubstituted ethylenes have a large inductomeric effect, which is brought into play under the influence of approaching ions or polar molecules at the moment of reaction. This statement is confirmed by the increase in the relative rates of bromine addition to ethylene and its methylated derivatives [126]:

Alkene	$CH_2=CH_2$	$CH_3CH=CH_2$	$(CH_3)_2C=CH_2$	$C(CH_3)_3=CHCH_3$	$(CH_3)_2C=C(CH_3)_2$.
Rate of addition	1.0	2.0	5.5	10.4	14.0

The ionisation potentials decrease in parallel [127,128]:

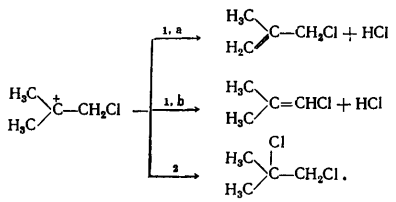
Alkene	$CH_2=CH_2$	$CH_3CH=CH_2$	$(CH_3)_2C=CH_2$	$CH_3CH=C(CH_3)_2$	$(CH_3)_2C=C(CH_3)_2$.
Ionisation potential	10.62	9.84	9.35	8.85	8.45

For 2-methylpropene, the first stage of chlorination may be represented by the following scheme:



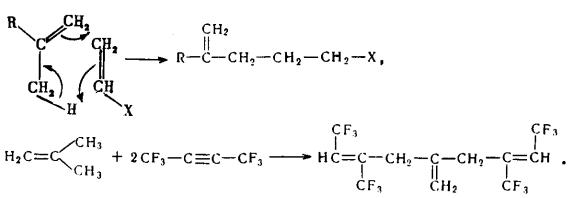
The intermediate carbonium ion is then stabilised in two main ways: (1) by elimination of a proton from adjacent alkyl groups with the formation of unsaturated monochlorides and the separation of a molecule of hydrogen chloride;

(2) by addition of a negative chloride ion to the positive centre of the carbonium ion with the formation of a saturated dichloride



Stabilisation of the carbonium ion in the first way is energetically less favoured by about 8 kcal mole^{-1}.[30] However, when there is a quaternary carbon atom at the double bond, this is the predominating route; according to Tishchenko, the approach of the Cl^- ion to the centre of the carbonium ion is sterically hindered, and this reduces the probability of stabilisation of the organic ion by the second route. In addition to an unsaturated monochloride of the allyl type, the reaction mixture always contains a small quantity of monochloride of the vinyl type. Tishchenko ascribes the preferential formation of the former to the high "proton-likeness" of the primary hydrogen of the methyl group.

This hypothesis was later confirmed experimentally by Morton and coworkers[129], who proposed a method for determining the relative acidity of unsaturated hydrocarbons and of the most "proton-like" hydrogen atom in the alkene. Moreover, the mobility of the allyl hydrogen has been confirmed by reactions in which monoalkenes are added to various activated unsaturated compounds[130-133].



A study of the microwave spectrum of 2-methylpropene[134] showed that the ordinary C–C bond in the latter is appreciably shortened in comparison with saturated compounds, which also indicates the acidity of the allyl hydrogen.

As a result of thorough investigations, Tishchenko[52-56] established that the presence of a quaternary carbon atom and polarisation of the double bond by substituents are necessary conditions for the anomalous chlorination of alkenes at low temperatures; using the reaction of phosphorus(V) chloride with ketones as an example, he confirmed these conclusions[53].

With the object of eliminating side-reactions due to the liberated hydrogen chloride (addition to the initial and final products[56]), a method of chlorination in the presence of sodium hydrogen carbonate, which readily reacts with hydrogen chloride, has been proposed[54,56]. Aschan's hypothesis[135] that sodium hydrogen carbonate catalytically promotes the elimination of hydrogen chloride from the initial dichloride has been disproved[56]. For example, 2,3-dichloro-2-methylbutane does not react with the hydrogen carbonate even at 135°. The mechanism of low-temperature chlorination proposed by Tishchenko was later accepted also by advocates of "substituting" chlorination[136]. The work of Tishchenko and coworkers on the chlorination of terpenes[30,137-140], many of which contain a quaternary carbon atom at a double bond, provided convincing proof of the views he developed on the mechanism of anomalous chlorination of alkenes.

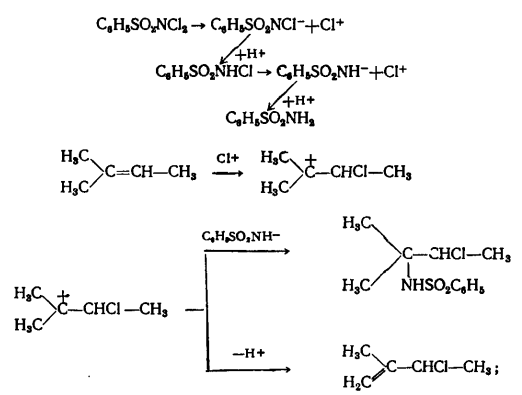
Other papers also show that schemes based on the heterolytic mechanism are widely applicable[141].

Some workers have expressed doubts about the Ingold–Tishchenko mechanism for the chlorination of alkenes[142,143], at least as applied to the chlorination of alkenes in non-polar media, where it was considered there were no grounds for assuming the existence of carbonium ions and ions of the halogenating agent.

The results of mass-spectrometric determinations of ionisation potentials of various compounds in solutions and gases show that this criticism is not valid[144]. Moreover, the heterolytic mechanism does not require that the addend should be ionised before the reaction[145].

Tishchenko's hypothesis that there is steric hindrance to the approach of the chloride anion to the centre of the carbonium ion has been denied without proof by Esafov[142]. Results of later investigations in this field[37] have shown that this criticism is not valid; the rapid addition of chlorine to alkenes (ethylene, propene, 2-methylpropene, styrene, and cyclohexene) at low temperatures in a condensed phase was explained by a reduction in steric hindrance.

Impressive arguments in favour of the steric-hindrance hypothesis in anomalous halogenation reactions have also been put forward by Isagulyants and Balashova[146-148], who studied the chlorination of alkenes with a quaternary carbon atom at the double bond by molecular chlorine and *NN*-dichlorobenzenesulphonamide. They showed that the yield of the anomalous chlorination product depends on the size of the halogenating-agent anion. Thus, in the chlorination of 2-methylbut-2-ene with *NN*-dichlorobenzenesulphonamide[147], the mechanism may be represented as follows:

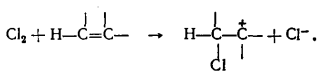


the main reaction product is the unsaturated 2-chloro-3-methylbut-2-ene. Because of the large bulk of the anion of the chloroamide compared with the chloride anion, only 1% of the 2-methylbut-2-ene reacts to form an addition product with the chloroamide, that is, 10–15 times less than with molecular chlorine[42]. Under the same conditions, the action of *NN*-dichlorobenzenesulphonamide on normal pentenes leads mainly to addition products[147].

The results of the chlorination of 3-chloro-2-methylbut-1-ene with *NN*-dichlorobenzenesulphonamide in a mixture

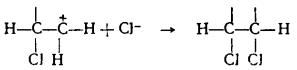
of methyl and ethyl alcohols are also satisfactorily interpreted by the steric-hindrance hypothesis [147].

Taft [145] presents a somewhat different scheme for the heterolytic mechanism in the anomalous chlorination of alkenes. According to Taft, the first stage, which determines the reaction rate, is electrophilic attack on the alkene with the formation of a carbonium cation and a chloride anion as in the Ingold–Tishchenko scheme,

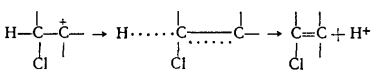


The intermediate carbonium ion reacts by two routes:

a. with the addition of a chloride anion



b. with elimination of a proton



The ratio of the amount of addition products to the amount of unsaturated monochlorides is determined by factors that affect the rates of addition and substitution. This ratio depends on the structure of the intermediate carbonium ion, and also on the reaction medium and the temperature.

Using published experimental results on the chlorination of various alkenes, Taft [145] established a relationship between the yield of unsaturated chloro-derivatives and the number of hydrogen atoms attached to carbon atoms in the α-position to the centre of the carbonium ion (Table 1).

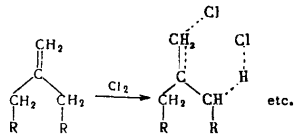
According to Taft, the dependence of the ratio of addition products to substitution products on the number of hydrogen atoms results from a hyperconjugation type of resonance [149,150]. The greater number of possible resonance structure in the chlorination of 2-methylpropene compared with ethylene means that the carbonium ion formed from 2-methylpropene may be more effectively transformed into a stable state than the ion obtained from ethylene. By analogy [151], this should reduce the ratio of the rates of addition and substitution, that is, at low temperatures the chlorination of 2-methylpropene leads to the formation of large amounts of unsaturated monochloride but ethylene mainly reacts to add on chlorine. This hypothesis of Taft on anomalous reactions is not confirmed by the general principles of electrophilic addition to alkenes.

Ingold [152], in analysing a communication of Robertson, concluded that in additions to alkenes the inductive effect of alkyl groups, and not the Baker–Nathan effect with participation of hydrogen, has the greatest influence on the reaction rate. Moreover, results have been published that do not generally favour the hyperconjugation effect [153–156].

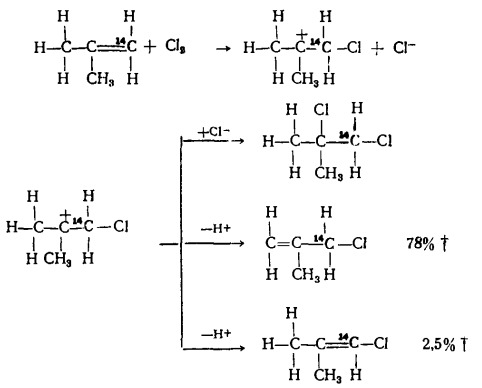
TABLE 1.

No. of hydrogen atoms	Substitution, %	Addition, %
2—3	0—35	60—100
4—5	10—60	40—90
6—7	70—85	10—30
8	93	7

In addition to the mechanisms given above for the chlorination of alkenes with a quaternary carbon atom at the double bond, synchronous cyclic and non-cyclic type mechanisms have been proposed, in which attack on the alkene molecule by a positively charged chlorine atom is accompanied simultaneously by reaction of a negatively charged chlorine atom with a protonated hydrogen atom [157,158]:



The papers of Reeve and coworkers mentioned above are of great interest for the elucidation of the mechanism of anomalous chlorination [45,46]. Their experimental results lead to a mechanism for the chlorination of 2-methylpropene similar to Tishchenko's mechanism:



The results of kinetic studies of the low-temperature chlorination of individual branched and straight-chain alkenes and their mixtures also indicate that these reactions are heterolytic [158–160].

Analysis of the kinetic results shows that substitution and addition reactions of chlorine with alkenes are parallel reactions of the same order and with the same common polar intermediate complex.

V. REACTION OF ALKENES CONTAINING A QUATERNARY CARBON ATOM WITH HYPOHALOGEN ACIDS

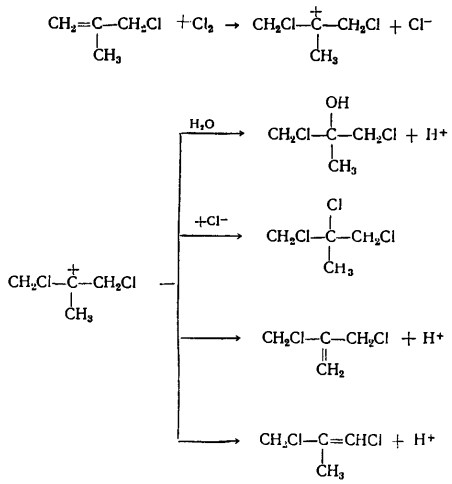
The addition of hypochlorous acid to unsaturated hydrocarbons was first studied by Markovnikov, who established the rule that bears his name [161]. Saytzeff [162], who studied the reaction of hypochlorous acid with butene, also found that the halogen adds to the carbon atom with the greatest number of hydrogen atoms, and the hydroxy-group to the carbon atom with the least number. On the other hand, Henry found that hypochlorous acid adds to propene and 2-methylpropene in the reverse manner [163]. Butlerov [164], who assumed that the product of the reaction of 2-methylpropene with hypochlorous acid was 2-chloro-2-methylpropan-1-ol, confirmed Henry's results, which were later shown to be erroneous.

Michael [165] repeated Henry's experiments and showed that the product of the reaction of hypochlorous acid with propene is 1-chloro-propan-2-ol, thus confirming the

† Yield based on chlorine.

validity of Markovnikov's rule. This conclusion was confirmed by Krasuskii [166,167], who showed that propene chlorhydrin contains ~ 68% of 1-chloropropen-2-ol, and 2-methylpropene chlorhydrin, not less than 78% of 1-chloro-2-methylpropan-2-ol. Quantitatively, these results differ somewhat from those reported by other workers for the addition of hypochlorous acid to propene [168] and 2-methylpropene [169-172].

Later papers are mainly devoted to a study of the mechanism of these reactions. Burgin and coworkers [136], who studied the action of chlorine water on 2-methylallyl chloride, explained the composition of the final products by the initial formation of a positively charged carbonium ion complex, which is then stabilised in several ways:



At 30° the yield of 1,3-dichloro-2-methylpropan-2-ol is 70%, and 10% of allyl and vinyl substitution products is formed. Other nucleophilic solvents may be used as the "active" medium instead of water. Thus, the action of chlorine [173] and bromine [174] on ethylene hydrocarbons in the presence of ethylene oxide leads mainly to the formation of $\beta\beta'$-dichloro- and $\beta\beta'$-dibromo-substituted ethers [173,174]. Besides these ethers, other products are obtained which indicate that the mechanism of this reaction is in principle similar to the mechanism for the chlorination of alkenes in an aqueous medium.

By means of the reaction of aromatic compounds with hypobromous acid, it has been shown that a bromine cation participates in brominations in aqueous solutions [175-177]; the rate of these reactions is proportional to the concentration of hydronium ions [108].

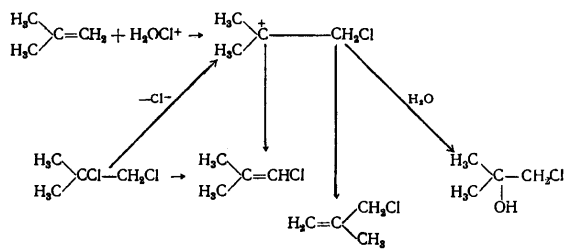
$$\frac{d[\mathrm{BrOH}]}{dt} = k[\mathrm{A}][\mathrm{BrOH}][\mathrm{H_3O^+}],$$

where [A] is the concentration of the organic compound. The concentration of the bromine cation is related to [BrOH] by the equation:

$$k_p[\mathrm{BrOH}][\mathrm{H_3O}] = [\mathrm{BrOH_2^+}].$$

The existence of a bromine cation was deduced from kinetic results obtained in the chlorination with hypochlorous acid of organic compounds [178,179]. Later, the experimental results on which the hypothesis of a chlorine cation is based were subjected to criticism [180].

Using an isotope dilution method at 45°, de la Mare and coworkers [181] separated 11.9% of 3-chloro-2-methylprop-1-ene and 0.4% of 1-chloro-2-methylprop-1-ene from the reaction products obtained by the action of hypochlorous acid on 2-methylpropene. A somewhat larger total of unsaturated monochloro-derivatives (16%) was obtained by the hydrolysis of 1,2-dichloro-2-methylpropane under comparable conditions. From these results the authors conclude that identical carbonium ions are formed as intermediates when hypochlorous acid acts on 2-methylpropene and in the hydrolysis of 1,2-dichloro-2-methylpropane:



on hydrolysis	6%	10%	84%
on addition	0.4%	12%	87.6%

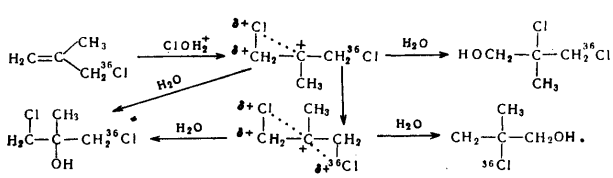
This hypothesis is in good agreement with the results of spectrographic [74,182] and cryoscopic studies [75] on solutions of tertiary alcohols and the corresponding alkenes in sulphuric acid. Thus, Gold and coworkers [74,75,183] showed that when $\alpha\alpha$-diphenylethylene is dissolved in sulphuric acid, a carbonium ion is formed identical with that obtained by similar treatment of 1,1-diphenylethanol:

$$(C_6H_5)_2C{=}CH_2 + H_2SO_4 \rightarrow (C_6H_5)_2CH_3C^+ + HSO_4^-,$$
$$(C_6H_5)_2CH_2COH + 2H_2SO_4 \rightarrow (C_6H_5)_2CH_3C^+ + H_3O^+ + 2HSO_4^-.$$

Later, the trimethylmethylium ion was obtained from 2-methylpropene and t-butyl alcohol by analogous methods [182]:

$$(CH_3)_2C{=}CH_2 \xrightarrow{+H^+} (CH_3)_3C^+ \xleftarrow[(-H_2O)]{+H^+} (CH_3)_3COH.$$

The preferential formation of unsaturated chloro-derivatives of the allyl type in comparison with vinyl derivatives (30 : 1) by the action of hypochlorous acid is explained [184] by internal interaction between the centre of the carbonium ion and the chlorine atom, as described by Roberts and Kimball [84]. Ballinger and de la Mare [185] studied the addition of hypochlorous acid to 2-methylallyl chloride containing the labelled atom ^{36}Cl and confirmed the hypothesis that the centre of the carbonium ion interacts with the halogen on the adjacent carbon atom by the partial displacement of ^{36}Cl from position 3 to position 2:



A similar migration of the chlorine atom was also observed in the reaction of hypochlorous acid with allyl chloride [186]. However, in the chlorination of allyl alcohol with molecular chlorine, the assumed interaction of the hydroxyl group with the positively charged carbon atom was not accomplished by migration of the hydroxyl group

to the centre of the carbonium ion [187], although that such a migration is possible in principle has been shown by the rearrangement of 1-phenylallyl alcohol to 3-phenylallyl alcohol in a mixture of dioxan and water (60:40 vol.%) in the presence of perchloric acid at 0°. [188]

The observations of de la Mare and coworkers [189] are important in considering the reasons for the elimination of a proton from alkyl groups adjacent to the centre of the carbonium ion with the formation of anomalous products; these workers found that treatment of [3-^{36}Cl]-2,3-dichloroprop-1-ene with hypochlorous acid leads to the formation of substitution products (3.7% of *cis*- and 4.3% of *trans*-1,2,3-trichloropropene). These results are in agreement with an earlier statement [53] that anomalous products are formed in chlorination not only by alkenes with a quaternary carbon atom at the double bond, but also by unsaturated compounds in which only one of the carbon atoms at the double bond does not have a hydrogen atom.

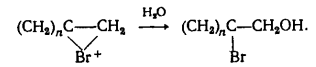
This analogy indicates the similarity between the mechanisms of chlorination and hypochlorination of alkenes, at least in the first stage when a carbonium ion is formed. This has been confirmed by other examples [47,191,192]. It is well known that normal alkenes react with chlorine at ordinary or slightly increased temperature to form only addition products. The action of hypochlorous acid on but-2-ene [190] and 2-methylpent-3-ene [191] also leads to addition at the double bond, but under similar conditions 2,4-dimethylpent-2-ene and diisobutylene give unsaturated monochlorides as the main products [191]. Umnova [191] explained the mechanism of the formation of substitution products in these reactions by L'vov's scheme, which includes initial additions of hypochlorous acid to the double bond followed by elimination of a molecule of water. We have dealt with the defects of this scheme in the section above on the chlorination of alkenes.

The action of hypobromous acid on acyclic unsaturated hydrocarbons leads to the formation of bromhydrins; the order of addition is mainly the same as that in hypochlorination. For example, the reaction of hypobromous acid with 2-methylpropene gave an addition product in 77% yield containing not less than 97% of 1-bromo-2-methylpropan-2-ol and 3% of the isomer, 2-bromo-2-methylpropan-1-ol [192,193].

A comparative study of the reaction of hypochlorous acid with allyl bromide and the reaction of hypobromous acid with allyl chloride [194] in a water–dioxan mixture showed that the solvent materially affects the composition of the products of the reaction, in which a halogen atom of the starting alkene migrates to the central carbon atom. The change in the composition of the reaction products can be explained fairly satisfactorily by a mechanism based on the formation of an intermediate carbonium ion.

Bodot and Jullien give an interesting theoretical explanation of orientation in the addition of electrophilic agents to alkenes [195]; using the method of Smith and coworkers [196], they calculated the relative stability of possible carbonium ions and showed, for example, that in the reaction of hypochlorous acid with 2-methylpropene the carbonium ion structure $(CH_3)_2\overset{+}{C}CH_2Cl$ is energetically more favoured than the structure $(CH_3)_2CClCH_2$.

However, in the hypohalogenation of cycloalkenes the order of addition is, as a rule, not so rigid as in the electrophilic addition of HOX to acyclic unsaturated compounds. Thus, in the hypobromination of methylenecycloalkenes the order of addition is reversed [192,193]. Traynham and Pascual [193] attempted to explain this orientation in the addition of hypobromous acid to methylenecycloalkenes by the formation of a bromonium ion with subsequent attack of a water molecule on the secondary carbon atom:



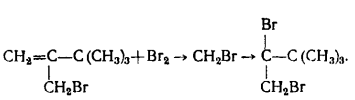
VI. REACTIONS OF ALKENES BRANCHED AT THE DOUBLE BOND WITH BROMINE AND INTERHALOGEN COMPOUNDS

The action of bromine, iodine, and interhalogen compounds on alkene compounds has mainly been studied with reference to normal compounds [113-122,197-202].

In a review [203], Dombrovskii lists the substitution reactions that occur in the halogenation, sulphonation, nitration, alkylation, acylation, and azo-coupling of both alkenes and aromatic compounds. In this review, the reactions of bromine and interhalogen compounds with unsaturated compounds having a quaternary carbon atom at the double bond are compared with the corresponding chlorination reactions.

As early as 1879, Butlerov observed the liberation of hydrogen bromide, and therefore the formation of substitution products, in the bromination of triisobutylene [204].

Hydrolysis of the products of the reaction of bromine with 2-methylbut-2-ene also showed the presence of unsaturated monobromides in the reaction mixture [205,206]. Later, Favorskii [207] established that the reaction mixture obtained by the bromination of isopentene contains t-pentyl bromide, with dibromo- and tribromo-derivatives of 2-methylbut-2-ene. With increase of bromination temperature, unsaturated bromo-derivatives of methylbutene were formed [208]. The dibromo- and tribromo-derivatives were the main products of the action of bromine on 2,3,3-trimethylbut-1-ene, when the reagents were cooled with an ice–salt mixture [207]. However, a mixture of saturated and unsaturated monobromides were separated from the low-boiling fractions. The formation of unsaturated monobromides was explained by L'vov's scheme for anomalous chlorination [9-11]. The formation of tribromo-derivatives was considered to be due to the reaction of bromine with the unsaturated monobromide which is partly formed:



It was also noted that *unsym*-dineopentylethylene [4,4-dimethyl-2-neopentylpent-1-ene] reacts with bromine with liberation of hydrogen bromide [209].

Esafov [210] observed considerable liberation of hydrogen bromide in the determination of the bromine numbers of di- and tri-isobutylene, and also of diene hydrocarbons with branching at the double bond. A thorough analysis of the bromination products of 2-methylpropene at 0° was first carried out by Pogorzhel'skii [211]. The main reaction product was 1,2-dibromo-2-methylpropane, that is, the addition product; t-butyl bromide and polybromo-derivatives of 2-methylpropene were also separated. Saponification of the fraction boiling below 100° failed to convert 0.3 g of bromo-derivatives (out of 4.4 g) into alcohols, and this

portion was assumed to consist of unsaturated monobromide. In later papers on the bromination of 2-methylpropene to obtain dibromo-derivatives, the formation of unsaturated monobromides is not mentioned[212,213]. However, since t-butyl bromide is formed, it may be assumed that the bromination of 2-methylpropene[210] is accompanied by the formation of 2-methylallyl bromide or dimethylvinyl bromide and hydrogen bromide. The latter further reacts with the starting 2-methylpropene.

The liberation of hydrogen bromide has also been noted in the bromination of 2-methylpropene in the presence of calcium halide, which catalyses additions to alkenes[214].

It was later shown[215] that bromination of an excess of liquid 2-methylpropene at -10°, either directly or in the presence of a non-polar solvent, is accompanied by the formation of up to 20% of allyl and vinyl substitution products. The yield of unsaturated monobromides falls to 5.5–6% if the experiment is carried out with stoichiometric quantities of the reagents.

If this reaction is carried out at a very low temperature (-154°), as in the chlorination of 2-methylpropene in a condensed phase[37], only addition products are formed[216].

In the gas-phase bromination of 2-methylpropene at 300–350° in an atmosphere of nitrogen, up to 50% of 2-methylallyl bromide and 20% of dimethylvinyl bromide are formed[18]; the remaining products are t-butyl bromide (7%) and polybromides (20%).[18] Under these conditions the reaction is probably of the free-radical type, and a sharp increase in the yield of 2-methylallyl bromide and dimethylvinyl bromide is probably due to replacement of hydrogen atoms according to Semenov[51]. It is well known, for example, that in the halogenation of alkenes with *N*-bromosuccinimide[217] and *N*-bromoacetamide[218,219], hydrogen in methyl and methylene groups is readily replaced by bromine. These reactions are accelerated by heat and by ultraviolet light[220], and also by the addition of peroxides[221]; the presence of peroxides promotes the formation of unsaturated monobromo-derivatives, while 4-t-butylpyrocatechol, an inhibitor of radical reactions, increases the yield of addition products.

Although the halogenation of alkenes by *N*-bromoacetamide is carried out in the presence of hydrobromic acid, like low-temperature bromination, the reaction is heterolytic, since here the double bond of the alkene is attacked by molecular bromine[219]:

$$AcNHBr + HBr \rightleftarrows AcNH_2Br^+ + Br^-;$$
$$AcNH_2Br^+ + Br^- \rightleftarrows AcNH_2 + Br_2.$$

Novikov and coworkers[222] examined published information on the halogenating properties of organic compounds containing positive halogen and concluded that *N*-bromosuccinimide can react with alkenes both by an ionic and by a homolytic mechanism.

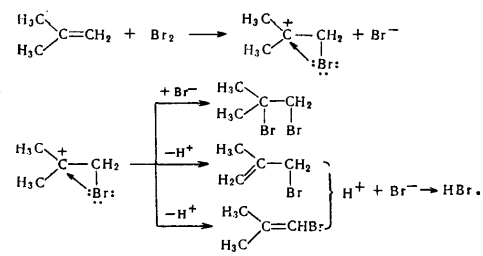
Tishchenko and Yarzhemskaya[223] studied the bromination of 2-methylbut-2-ene and 3-chloro-2-methylbut-2-ene at low temperatures in the presence of sodium hydrogen carbonate; they showed that, in contrast to chlorinations[41], only a small part of the bromine reacts to form unsaturated monobromides.

Comparison of published information on low-temperature chlorination[42,46] and bromination[215,223] of alkenes with branching at the double bond shows that while chlorination leads mainly to the formation of anomalous products, in bromination the predominating reaction is addition (Table 2).

TABLE 2.

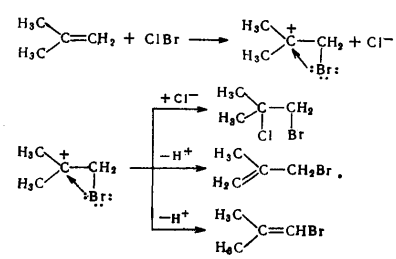
Alkene		Yield of anomalous products, %	Yield of normal products, %	References
H_3C H_3C $C=CH-CH_3$	chlorination	70—80	10—15	42
	bromination	15	85	223
H_3C H_3C $C=CCl-CH_3$	chlorination	80	10	42
	bromination	15	85	223
H_3C H_3C $C=CH_2$	chlorination	82.4	17.6	46
	bromination	20	60	215

The mechanism of the reaction of bromine with alkenes containing a quaternary carbon atom may be represented by the Ingold–Tishchenko scheme, a halogen atom reacting internally with a carbonium centre:



According to Temnikova[224], the composition of the reaction products of halogens with alkenes having a quaternary carbon atom is determined by the nature of the nucleophilic component of the halogenating agent. However, the results of low-temperature bromination and chlorobromination of liquid 2-methylpropene have shown that the nucleophilic properties of the halogen have no appreciable effect on the yield of anomalous chlorination products[215].

Published information[225–229] shows that bromine chloride adds to unsaturated compounds by an ionic mechanism; Br^+ attacks the double bond of alkenes to form an intermediate carbonium ion. The mechanism of chlorobromination may thus be represented by the following scheme:



Comparison of the scheme for the mechanism of bromination of 2-methylpropene with this scheme for chlorobromination shows that both reactions proceed through an identical intermediate carbonium ion. If it is assumed that the nucleophilic centre of the halogen plays a predominating part in anomalous halogenation reactions, then the yield of monobromides should be higher in chlorobromination than in bromination. However, experimental results show that in both the yield of unsaturated monobromo-derivatives is ~ 20%.

In the gas-phase chlorobromination of 2-methylpropene at 150° in a flow-through system[230], the yield of 2-methylallyl bromide is 41.5%, that is, somewhat lower than in the

gas-phase bromination of 2-methylpropene at 300°.[18] From this it follows that the anionic centre of the halogen has no appreciable effect on the composition of the products of halogenation of alkenes with a quaternary carbon atom at the double bond.

The authors of the present review[231] have put forward the hypothesis that the main reason for the elimination of a proton from alkyl groups in the α-position to the carbonium ion centre, and therefore for the formation of anomalous halogenation products, is the high degree of localisation of the positive charge at the centre of the organic cation formed as a result of electrophilic attack on the alkene[231]. On the other hand, delocalisation of the positive charge, due to the high polarisability of the electrophilic part of the reagent attached to the carbon atom in the α-position to the centre of the organic cation, hinders the elimination of a proton; as a result, the carbonium ion is stabilised by the addition of a halide ion to the positively charged carbon, and dihalo-derivatives are formed as final adducts. Here the reaction rate also depends on the nucleophilic properties of the halide anion[115].

Interaction of the centre of the carbonium ion with the added halogen probably occurs not in a chain-like manner but spatially, according to Roberts and Kimball[84], or de la Mare and coworkers[184,185]. This hypothesis was checked experimentally by introducing atoms of different inductomeric polarisability into the α-position of the alkene being chlorinated. Results obtained in the chlorination of 2-methylallyl chloride, 2-methylallyl bromide and 2-methylallyl iodide confirm the hypothesis; as the inductomeric polarisability of the halogen atom at the carbon atom in the α-position to the carbonium ion increased, the yield of anomalous chlorination products fell from 50% to 0%[231] (see Table 3).

Internal interaction between a positively charged centre and electronegative or strongly polarised groups at the α-carbon atom may lead to the formation of a new bond. On the basis of the foregoing hypothesis, the formation of halo-lactones when bromine or chlorine acts on the sodium salt of dimethylmaleic or dimethylfumaric acid may be represented by the following scheme[232]:

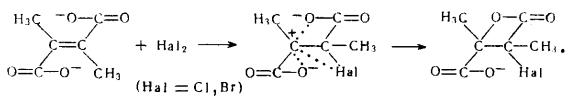
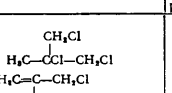
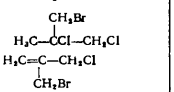
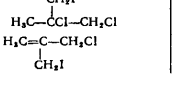


TABLE 3. Results of the low-temperature chlorination of unsaturated monohalo-derivatives of 2-methylpropene.

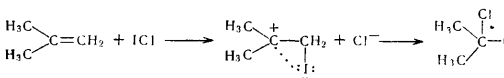
Starting alkene	Proposed structure of intermediate carbonium ion	Possible final adducts*	Yield of reaction products, %
			30
			50
			60
			11.7
			82.5
			0

* The total isomers of unsaturated halo-derivatives are arbitrarily denoted by a single formula.

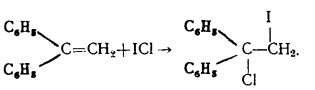
In the first example, because of its greater inductomeric polarisability, the added bromine atom probably partially delocalises the charge on the intermediate organic cation, which further stabilises the latter and thereby prevents the formation of a new lactone bond between the carbon atom and the carboxyl group.

A number of other results are also in good agreement with interpretations that take account of the effect of the polarisability of the electrophilic centre of the reagent.

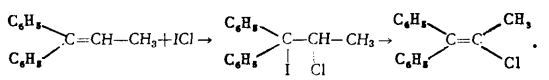
Thus, in the reaction of 2-methylpropene with iodine chloride, the positive charge on the carbon atom is delocalised by the added iodine atom; for this reason, 2-methylallyl iodide was not formed and 2-chloro-1-iodo-2-methylpropane was the sole reaction product[233]:



The addition of iodine chloride to propene[60,234], allyl alcohol and its esters[235], styrene[236], and 1,1-diphenylethylene[237] confirmed the validity of this order of orientation of the iodine chloride molecule, for example:



However, as Temnikova and coworkers have shown, this order may be changed by other substituents[237]. Thus, the production of 2-chloro-1,1-diphenylprop-1-ene when iodine chloride reacts with 1,1-diphenylprop-1-ene was explained by the initial formation of 2-chloro-1-iodo-1,1-diphenylpropane, which eliminates hydrogen chloride at the moment of reaction:



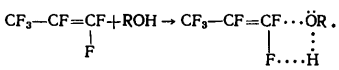
Recently, the effect of the magnitude of the charge on the positively charged carbon atom on the stabilisation route of the carbonium ion was studied in the low-temperature bromination of liquid 2-methylpropene in the following solvents of varying polarity: 2-methylpropene, chloroform, 1,1-dichloroethane, 1,2-dichloroethane, t-butyl chloride, and nitroethane[238]. It was shown that the total yield of 2-methylallyl bromide and dimethylvinyl bromide, and therefore the rate of elimination of a proton from the alkyl groups of the carbonium ion, decreases in proportion to the increasing dipole moment of the solvent; the yield of unsaturated monobromides decreases from 24% with 2-methylpropene to zero with nitromethane in the solvent order given above.

A study of the effect of solvent : alkene ratio on the composition of the products of the low-temperature halogenation of alkenes with a quaternary carbon atom at the double bond showed that a reduction in the concentration of alkene in the solvent leads to a decrease in the yield of allyl and vinyl substitution products[238].

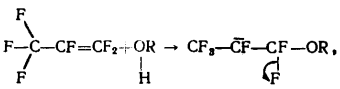
These results show that the ionic charge due to a strongly polar solvent may be reduced by increasing the quantity of less polar solvent while other reaction conditions are kept constant.

An interesting analogy is observed in reactions of alkenes with electrophilic reagents and of fluoroalkenes with nucleophilic compounds[239]. In reactions of perfluoroalkenes with nucleophilic reagents, the difluoromethylene group, which has an induced partial positive charge, is the object of nucleophilic attack; perfluoro-2-methylpropene reacts more readily with nucleophilic agents than perfluoropropene.

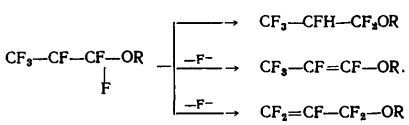
On the other hand, because of the positive inductive effect of alkyl groups, the methylene group of alkenes has excess electron density and is the object of electrophilic attack; the activity of alkenes in reactions with electrophilic reagents increases with the number of methyl groups at the double bond[126]. There is another interesting analogy between the reactions of alkenes and fluoroalkenes. When perfluoroalkenes are subjected to nucleophilic attack, replacement of fluorine atoms in the vinyl, and frequently the allyl, position is observed as well as addition at the double bond[240-245]. It has been suggested[243] that the nucleophilic reagent is linked with the electrophilic perfluoroalkene molecule in a four-membered transition state, which is stabilised by the intramolecular formation of a hydrogen bond[243]:



A somewhat different explanation of the mechanism of these reactions has also been put forward: the initial step in the reaction is considered to be attack by an anion; this leads to the formation of an intermediate carbanion,



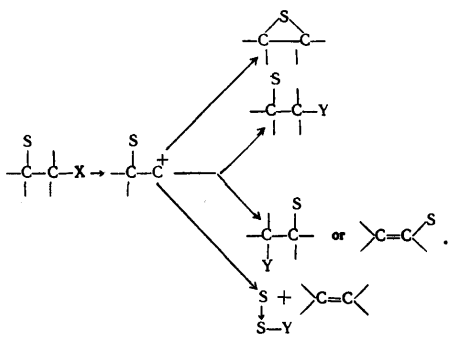
which is then stabilised by the addition of a proton or the elimination of a fluoride anion:



Under the same conditions, the relationship between addition, allyl substitution, and vinyl substitution depends on the structure of the perfluoroalkene and on the mobility of the unshared pair of the nucleophilic agent[239].

The main conditions that determine the stabilisation route of the carbonium ion, and therefore the composition of the products, in the electrophilic low-temperature halogenation of alkenes, are also, as pointed out above[52-56], the structure of the alkene and the mobility of the unshared pair of the attacking electrophilic agent[215,231]. Additions to fluoroalkenes and to alkenes are therefore similar.

A change in the mobility of the electron pairs of atoms at the carbon atom in the α-position to the centre of the carbonium ion, should also affect the composition of the final products in fragmentation reactions, in which the intermediate carbonium ion formed by displacement of some substituent from the organic compound may be stabilised in several ways[246-248]:



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QUINONE DIAZIDES AND *p*-IMINOQUINONE DIAZIDES

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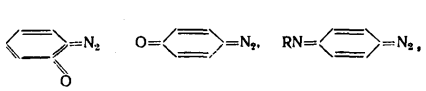
I. INTRODUCTION

para-Substituted and *para*- and *ortho*-hydroxy-substituted diazonium salts have characteristic properties; when treated with alkaline agents they form compounds of the type:



although most diazonium salts form diazoates. The following names are used in the literature for these compounds: diazoanhydrides, diazoquinones, diazo-oxides, and quinone diazides for the oxo-derivatives, and *p*--diazoimines (*p*-diazoimides if R is an acyl group), *p*-iminodiazoquinones, and *p*-iminoquinone diazides (or *p*-imidoquinone diazides) for the imino-derivatives. We shall call these compounds quinone diazides and *p*-iminoquinone diazides (or *p*-imidoquinone diazides)†.

Because of their unusual properties, these compounds occupy a special place in the chemistry of the diazo-compounds. *p*-Iminoquinone diazides and quinone diazides are theoretically interesting, as they may be regarded as occupying an intermediate position between aliphatic diazo-compounds and aromatic diazonium salts. Moreover, these compounds are widely used industrially for the synthesis of photosensitive dyes. In the laboratory, many compounds otherwise difficult to obtain are synthesised from *p*-iminoquinone diazides and quinone diazides.

Although good reviews have been published on the structures and properties of diazonium salts [1,2] and of aliphatic diazo-compounds [3-5], there is no review on the present state of the chemistry of *p*-iminoquinone diazides and quinone diazides. Since a large number of papers has appeared, particularly in recent years, on the reactions and structures of these compounds, it seemed useful to systematise the extensive information that has accumulated. A review of the literature on the synthesis, properties, and structure of quinone diazides and *p*-iminoquinone diazides (*p*-imidoquinone diazides) is given below.

II. PREPARATION OF *o*- AND *p*-QUINONE DIAZIDES AND *p*-IMINOQUINONE DIAZIDES

A. Preparation of Quinone Diazides

Methods used for the preparation of diazo-ketones and methods for synthesising diazonium salts may both be used for the synthesis of quinone diazides.

The following are five different methods of synthesis: (1) diazotisation of aminophenols; (2) diazotisation of aromatic amines not containing hydroxyl groups, with subsequent introduction of a hydroxyl group into the diazonium salt; (3) from phenols by introduction of a diazo-group; (4) from quinones, through *p*-toluenesulphonylhydrazones; (5) by the introduction of new substituents into a quinone diazide already synthesised.

It should be mentioned that each of these methods requires an acid medium at one stage, and therefore the synthesis of quinone diazides reduces to the preparation of the corresponding hydroxyaryl-diazonium salt with subsequent elimination of a molecule of acid from this salt.

A solid quinone diazide is readily formed by elimination of a molecule of acid from the diazonium salt, if the aryl group consists of a system of condensed benzene rings [6] or has negative substituents [7,8]; the solid quinone diazide is then precipitated when the diazo-solution is diluted with water. Sometimes the solution must be strongly cooled, or it must be neutralised [9-11]. If the diazide is poorly soluble in water, it may be extracted with benzene [12]. If the diazides are very soluble in water, special methods are used for their separation. Thus, Anderson and Roedel [13] obtained *p*-benzoquinone diazide in low yield by

† The second of these alternatives is usually favoured in the Russian text but the first has been employed in the translation (Ed. of Translation).

treating the diazonium chloride with silver oxide in alcohol, and cooling the solution to -70° after the addition of ether; *o*-benzoquinone diazide was first obtained by Anderson and Le Fevre, using the same procedure [14]. Stille and coworkers used an analogous method for the preparation of some *p*-benzoquinone diazides [15]. Later, *o*-benzoquinone diazide was obtained in high yield by treating dry *o*-hydroxyphenyldiazonium chloride with anhydrous sodium carbonate, the diazide being subsequently extracted by boiling ether or hexane [11].

1. Synthesis of quinone diazides by diazotisation of *o*- or *p*-aminophenols. Difficulties are encountered in the diazotisation of aminophenols by the usual methods, because of the readiness with which these compounds are oxidised, or because of their low solubility. For this reason, the diazotisation of aminophenols is often carried out under special conditions. The diazotisation proceeds most smoothly in organic solvents. Schmidt and Glitz were the first to diazotise the simplest aminophenols with nitrogen oxides in ether [16]. Hantzsch and Davidson later used this reaction for the diazotisation of unsubstituted aminophenols [10].

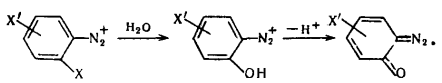
Diazotisation of aminophenols with sodium nitrite in a medium of concentrated organic acids proved to be a very convenient method, solutions of the corresponding diazonium salts being obtained in high yield [17-20]. The yield of the salt increases with the strength of the organic acid used as solvent [17,18]. In the diazotisation of some highly condensed or heterocyclic hydroxy-amines, good results are obtained with the use of dimethylformamide or glycol methyl ether as solvent [7].

When aminophenols are diazotised in the usual way with nitrite in hydrochloric acid solution, large amounts of oxidation products are obtained. Thus, diazotisation of aminonaphthols in aqueous acid gives the corresponding quinones and azo-dyes [21,22]. Aminophenols with positive substituents in the nucleus, for example, aminoresorcinol, are very strongly oxidised [23]. However, it has been shown that in dilute sulphuric acid the diazotisation of unsubstituted *o*- and *p*-aminophenols proceeds without complications [11]. Using this method, Ershov and Nikiforov [12] obtained a number of crystalline *p*-quinone diazides with alkyl substituents in positions 2 and 6.

The presence of electronegative substituents in the nucleus gives rise to a difficulty of another kind: diazotisation does not occur because of the poor solubility of these aminophenols in weakly acid solution. Although monohalo- and mononitroso-substituted aminophenols can be diazotised in the usual way [7,9,24], the introduction of additional negative substituents into the nucleus makes diazotisation impossible under ordinary conditions.

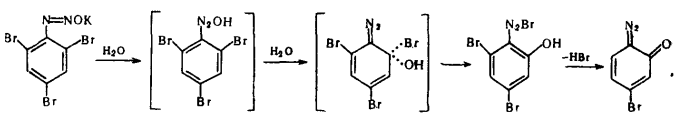
To overcome these difficulties, it has been proposed that oxidisable aminophenols should be diazotised with sodium nitrite in an aqueous solution not containing mineral acids but containing salts of heavy metals, $CuSO_4$,[6,25] $SnCl_2$,[26] etc.[1] Aminophenols with negative substituents are smoothly diazotised by nitrosylsulphuric acid in concentrated sulphuric acid [20,27]. Hodgson and Birtwell [20] showed that substituted aminophenols that cannot be diazotised by other methods because of oxidation, are readily diazotised in concentrated sulphuric acid without the addition of nitrite. In this way a diazonium salt was obtained from 1-amino-4-diazonaphth-2-ol, and the diazotisation of this amine was equally smooth in glacial acetic acid [20].

2. Synthesis from amines containing no hydroxy-groups. If the diazonium salt has a substituent in the *ortho*- or *para*-position to the diazonium group, under certain conditions (dilution of the diazo-solution with water or addition of bases) this substituent is readily exchanged for a hydroxyl group, and the hydroxyaryldiazonium salt formed is converted into the corresponding quinone diazide by the loss of a molecule of acid:



A nitro-group, halogen, sulpho-, or methoxyl group may be replaced by a hydroxyl group [1]. Orton, who was the first to make a systematic study of replacement of halogens by the hydroxyl group, found [28] that the reaction rate greatly depends on the structure of the diazonium compounds (Table 1).

The accumulation of negative substituents on the nucleus facilitates replacement. In the naphthalene series, replacement occurs much more readily than in the benzene series. Since potassium tribromophenyldiazoate is stable under the reaction conditions, Orton suggested that the diazohydroxide, and not the diazoate, takes part in the reaction [28]. According to Orton, an intermediate quinonoid transition state is formed:



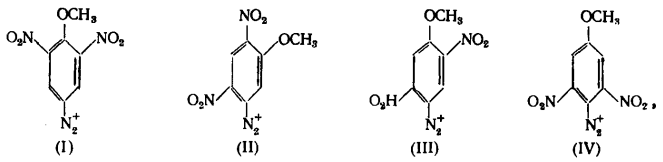
Much later, Mills noted that substitution occurs in the diazonium cation [29].

Meldola and coworkers made a detailed study of the replacement of substituents by hydroxyl groups and observed a number of special features in this exchange [30-35]. Meldola and Eyre showed that the nitro-group and halogens are eliminated as the corresponding anions [34]. For example, in the elimination of the nitro-group nitrous acid is formed in solution, and this can diazotise the starting amine [34]. This is the first description of what is called auto-diazotisation. These workers also showed that in concentrated hydrochloric acid the substituent is exchanged not for a hydroxyl group but for a chlorine atom [34]. In sulphuric or nitric acid, the acid anion is never exchanged for a substituent in the diazonium salt. Meldola and coworkers established [33,35] that two conditions are necessary for the replacement of a substituent by the hydroxyl group: the group replaced must be in the *o*- or *p*-position to the diazonium group and it must be activated by a nitro-group

TABLE 1.

Diazo-compound from	Chlorine eliminated in 24 hours, %	Diazo-compound from	Chlorine eliminated in 24 hours, %
2,4-Dibromo-1-naphthylamine	97	2,3,4,6-Tetrabromoaniline	74
2,4,6-Tribromo-3-nitroaniline	93	2,4,6-Tribromoaniline	64
2,4-Dibromo-5-nitroaniline	80	2,4,6-Trichloroaniline	63
1-Chloro-2-naphthylamine	76	2,6-Dibromoaniline	24
		2,4-Dichloroaniline	traces

in the *ortho*-position to it[35]. Thus, of the compounds I to IV:



(I) (II) (III) (IV)

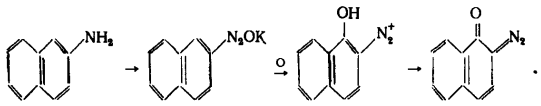
only I and III, which satisfy these conditions, are capable of exchanging a nitro-group or a methoxyl group for a hydroxyl group and undergoing conversion into quinone diazides. If the nitro-group and the alkoxyl group are in positions equally favourable for replacement, the nitro-group is replaced[35]. Continuing this work, Morgan and Evens showed that the nitro-group in the diazonium salt obtained from 2,4-dinitroaniline can also be replaced[36]. If conditions are equally favourable for the replacement of a halogen atom or an alkoxyl group by a hydroxyl group, the alkoxyl group is replaced[37]. If conditions are equally favourable for the replacement of an *o*- and a *p*-nitro-group, the *ortho*-group is preferentially replaced[36,38]. The tendency for the formation of *o*-quinone diazides is so great that in the diazotised 2,6-dichloro-4-nitroaniline molecule a chlorine atom and not a nitro-group is replaced by a hydroxyl group[39].

Hodgson and Birtwell showed[27] that if a substituted naphthylamine is diazotised in sulphuric acid containing the minimal quantity of water, the diazonium sulphates corresponding to the initial amine are formed[27]. However, if the diazo-solution is diluted, or if the diazotisation is carried out in acetic acid, or in a mixture of acetic and sulphuric acids, the corresponding substituent is replaced and diazides are formed[27]. These workers recommend that the diazotisation should be carried out with sodium nitrite in a mixture of sulphuric and acetic acids, or in glacial acetic acid, and that the diazide should be separated by diluting the solution with water or by neutralising it with ammonia or copper carbonate.

The formation of quinone diazides following the replacement of electronegative groups in the diazonium cation by a hydroxyl group is sometimes undesirable, for example, in Sandmeyer's reaction with diazonium salts obtained from 2,4-*x*-trinitro-1-naphthylamine (x = 3, 5, 7, 8)[40]. In order to avoid the formation of quinone diazide as a by-product, it has been proposed that Sandmeyer's reaction should be carried out in non-aqueous media with, for example, acetic acid saturated with hydrogen halide as solvent[41].

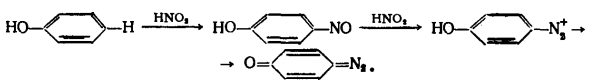
This reaction in which substituents are exchanged is of great importance in the azo-dye industry, since on coupling the hydroxyaryl-diazonium (*ortho*-isomers) salts formed are converted into hydroxyazo-dyes, which are capable of forming lakes with heavy metal cations. The synthesis of hydroxyazo-dyes incorporating a stage in which various groups are replaced by a hydroxyl group is described in many patents. The hydroxyaryldiazonium salts are then formed in solution only as intermediate products and the corresponding diazides are never separated. Detailed information on these patents is given in the monograph of Saunders[1].

The oxidation reaction, in which a hydrogen atom is replaced by a hydroxyl group, is a special case of the introduction of a hydroxyl group into the molecule of a diazonium compound. Bamberger[42-44] proposed this method of synthesising diazides; he oxidised diazoates obtained from 1- or 2-naphthylamines with potassium hexacyanoferrate(II) in alkaline solution:



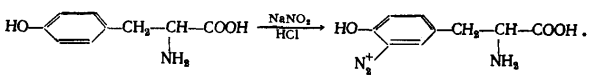
1,2- and 2,1-naphthoquinone diazides were obtained in high yield.

3. Synthesis of quinone diazides from phenols. In this method phenols or nitrosophenols are treated with nitrous acid in aqueous solution. Hydroxyaryldiazonium salts are first formed, and these are then converted to quinone diazides:



Although this method has been little studied, it is very promising, because it permits the preparation of quinone diazides directly from phenols, and it obviates the synthesis of aminophenols, which are not always accessible and are sometimes difficult to diazotise. This applies particularly to phenols with positive substituents.

The method is based on a reaction discovered by Weselsky[45], who treated phenol with nitrogen oxides and obtained hydroxyphenyldiazonium nitrate. The same salt was obtained in a similar way from nitrosophenol[46]. Morel and Sisley carried out the following reaction[47]:



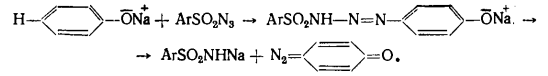
It was shown by azo-coupling that the yield of the diazo-compound is 80%. Phenols containing sulpho-groups[48] or chlorine[49] were also treated with nitrogen oxides, and the corresponding diazophenols were found in the reaction mixture. Nesmeyanov and Ioffe[50] showed that the presence of substituents of the first kind in the nitrosophenol nucleus promotes the formation of a quinone oxime structure and thereby prevents diazotisation. Nitrosonaphthols, which exist as naphthoquinone oximes, do not react with nitrogen oxides. From the results obtained it was concluded that nitroso-compounds react with nitrogen oxides in the benzenoid and not in the quinonoid form.

Nemodruk showed that when nitrous acid acts on salicylic acid carbon dioxide is liberated and diazophenol is formed in the solution in good yield[51]. If cyclic metal salts of salicylic acid are introduced into the reaction, the diazo-group enters the *para*-position to the hydroxyl group, and salts of 5-diazosalicylic acid are formed in nearly quantitative yield[52].

In recent years Tedder and Theaker developed a method for the preparation of hydroxyphenyldiazonium salts from phenols[53]. They showed that the greatest yield of diazo-compound is obtained when the reaction is carried out in aqueous solution with a molar ratio of starting materials (phenol: HCl: $NaNO_2$) of 1 : 4 : 14.5. The mixture is maintained at 0° for 20–40 h, and the yield of the diazo-compound is determined by azo-coupling. The yield largely depends on the nature of the phenol: the greater the acidity of the starting phenol, the lower the yield of the diazo-compound. It is assumed that nitrosophenols are formed as intermediates. Naphthols do not form diazo-compounds, as they are converted into quinoneoximes. If

the position *para* to the hydroxyl group is free in the phenol, the corresponding *p*-hydroxyphenyldiazonium compound is formed.

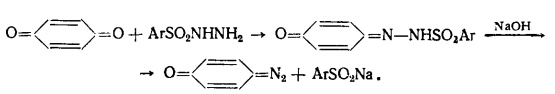
Tedder and Webster treated various phenoxides with *p*-toluenesulphonyl azide and obtained mixtures of azo--dyes[54]. They proposed the following scheme for the process:



The quinone azide couples with an excess of phenoxide to form the dye. If the diazide obtained couples slowly, it may be separated. This reaction provides a convenient method for the introduction of a diazo-group into phenols containing negative substituents which do not react with nitrogen oxides in acid solution.

The preparation of quinone diazides by treatment of compounds with nitrogen oxides has been used in industry. The preparation of 1,4-didiazo-anthra-9,10-quinone by treating anthraquinone with nitrosylsulphuric acid has been described in a patent[55].

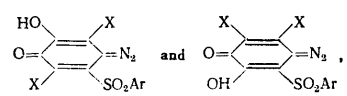
4. Synthesis of quinone diazides from quinones. Börche and Frank showed that treatment of quinones with aromatic sulphonyl hydrazides gives arylsulphonylazophenols $HO.C_6H_4N_2SO_2Ar$, which are also obtained from quinone azides and arylsulphonic acids[56-59]. When treated with mineral acids or alkalis, the arylsulphonylazophenols are decomposed into arylsulphinic acids and hydroxyphenyldiazonium salts (or the corresponding diazoates, according to Börche and Frank[56]). Later this reaction was used for the synthesis of aliphatic diazo--cations[59], and then Cava and coworkers[60] used it for the synthesis of cyclic diazo-ketones, including some quinone diazides. The reactions proceed according to the following scheme:



Using the method they had developed, Cava and coworkers[60] were the first to obtain the diazides corresponding to isatin and 9,10-phenanthraquinone; a previous attempt to obtain this compound by diazotisation of aminohydroxyphenanthrene was not successful[61].

The method of synthesising diazides from quinones became particularly valuable after Horner and Dürckheimer had proposed[62] a simple procedure for the preparation of *o*-quinones by the oxidation of aromatic diazo--compounds with chloroaniline or bromoaniline.

Reid and Dietrich made a detailed study of the synthesis of quinones through *p*-toluenesulphonyl hydrazones. They showed[63] that the hydrazones of aliphatic ketones decompose only in alkaline solutions, but quinone hydrazones decompose in both acid and alkaline solutions. The colour of the hydrazone is a rough indication of its stability: the more intense the colour, the lower the stability. It was also noted that if the oxidation potential of the quinone is sufficiently high, side-reactions occur in the preparation of the diazides. For example, compounds of the following type were obtained from halo-anils:



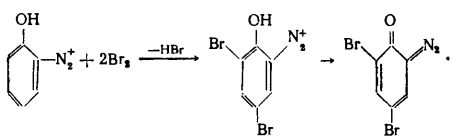
where X is a halogen atoms.

Reid and Dietrich[64] showed that the compounds obtained do not result from the secondary reaction of quinone diazides with arylsulphinic acid, but replacement of chlorine by an arylsulphinic acid residue occurs with the formation of a diazide from quinone *p*-toluenesulphonylhydrazones[64].

Horner and Dürckheimer studied[65] the reaction of various *o*-quinones of the benzene series with *p*-toluenesulphonyl hydrazide in order to determine which of the two non-equivalent quinone carbonyl groups takes part in the reaction. The results showed that in 4- or 5-substituted *o*-quinones the C=O group not conjugated with the substituent reacts with the hydrazide, but in 3- and 3,5-substituted quinones the reactive group is the carbonyl remote from the substituent in position 3. In these instances steric factors predominate over electronic factors.

The synthesis of quinone diazides has permitted the preparation of a large number of diazides with electropositive substituents[65].

5. Preparation of substituted quinone diazides. Only a few examples are known of the preparation of diazides by the introduction of new substituents into a previously synthesised diazide. In 1881 Bohmer[66] showed that when treated with bromine water, *o*- and *p*-benzoquinone diazides give 2-diazo-4,6-dibromo-*o*-benzoquinone and 4-diazo-2,6-dibromo-*p*-benzoquinone. The mechanism of these reactions has not been studied, but the author assumes that a diazonium cation takes part:



The reaction with hydroxyphenyldiazonium nitrate and hydrobromic acid proceeds in the same way; a nitrate ion formed in the first stage of the process oxidises the acid to bromine, which then brominates the diazide.

The halogen atom may replace other groups besides the hydrogen atom. Kollrepp[67] established that when bromine water acts on 3-chloro-5-diazo-2-oxocyclohexa-3,4-dienesulphonic acid, sulphurous acid is eliminated and 6-bromo-2-chlorobenzoquinone diazide [6-bromo-2--chloro-4-diazocyclohexa-2,5-dien-1-one] is formed[67].

It has been reported[68] that 6-bromo-4-sulphonaphtho--1,2-quinone 1-diazide is formed from 4-sulphonaphtho--1,2-quinone 1-diazide by the action of bromine in chlorosulphonic acid or sulphuric acid. However, in the naphthalene series this reaction sometimes leads to the oxidation of the diazide with elimination of diazoate. Thus, the action of bromine on 4-bromonaptho-1,2--quinone 2-diazide gives dibromonaphtho-1,2-quinone[69]; sometimes brominated naphthols are formed[70].

According to patent information[71-73], 1-diazo-2-naphthol--4-sulphonic acid can be nitrated and sulphonated. According to Ruggli and coworkers[68-72], the nitro-group (and probably also the sulpho-group) enters position 6 in the naphthalene ring.

All the reactions mentioned above are carried out in strongly acid solution, and there is reason to suppose that it is the diazonium, and not the diazide, form of the compounds that takes part in the replacement reaction.

Another example of substitution in the quinone-diazide ring is the conversion of diazides of the naphthalene series containing sulpho-groups; when these diazides are treated with sulphuryl chloride or chlorosulphonic acid, sulphonyl chlorides are formed, which give sulphonamides on treatment with amines [7,8,74-82].

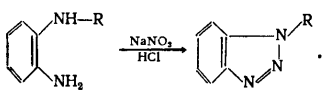
In recent years various examples of this reaction have been published in patents [74-82]. These sulphonamide derivatives of quinone diazides are of interest because they are widely used in the production of photosensitive materials.

Reid and Dietrich have succeeded in acylating a hydroxyl group in quinone diazides [64].

B. Preparation of *p*-Iminoquinone Diazides

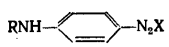
Only *para*-substituted diazonium salts form imino-quinone diazides (imidoquinone diazides). When treated with even weak alkaline agents (sodium acetate) *meta*--substituted diazonium salts lose the diazo-nitrogen and are converted into phenol derivatives, which immediately condense with another diazonium molecule [83].

In contrast to *o*-quinone diazides, *o*-iminoquinone diazides cannot be prepared, because diazotisation of *o*-phenylenediamines gives, instead of the diazonium salt, a precipitate of a colourless internal condensation product (benzotriazole derivative) [83]:

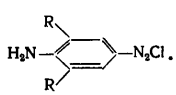


p-Iminoquinone diazides are much less stable compounds than quinone diazides, and there are therefore much fewer methods of preparing them. *p*-Iminoquinone diazides are mainly prepared by the action of alkaline agents on solutions of amino-substituted diazonium salts.

p-Iminoquinone diazides are formed only from *N*-substituted *p*-aminophenyldiazonium salts:



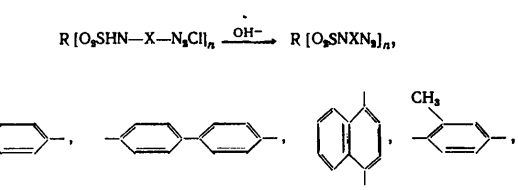
or from nuclear-substituted diazonium salts:



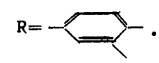
NaOH, NH_4OH, Na_2CO_3, $NaHCO_3$, or CH_3COONa may be used as the alkaline agent, according to the nature of the substituent R; sometimes the *p*-iminoquinone diazides may be separated by simply diluting the diazo-solution with water.

p-Iminoquinone diazide was first obtained by Ykuta [84], who prepared it in an impure state by treating the corresponding diazonium sulphate with ammonium hydroxide. Hantzsch investigated and described the compound [85]. Morgan and coworkers then found that *p*-iminoquinone diazides are formed by the action of a saturated solution of sodium acetate (or other alkaline agents) on diazotised *N*-substituted *p*-phenylenediamines, in which the substituent is an alkylsulphonyl [83], arylsulphonyl [86,87], or a mixed arylalkylsulphonyl group [88].

The reaction may be represented by the following general scheme [89]:

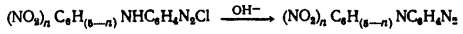


and *n* is the valency of the radical linked to the sulphonyl group; when $n = 1$, R = CH_3, C_6H_5, p-$CH_3C_6H_4$; when $n = 2$, R = $-CH_2-$, 1,3-phenylene; when $n = 3$,



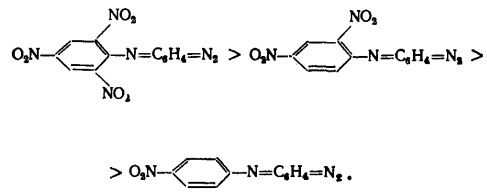
p-Iminoquinone diazides with substituents in the *ortho*- or *meta*-position to the diazo-group are formed without the addition of alkaline agents by simply diluting the diazo--solution with water [90].

p-Iminoquinone diazides are also formed fairly readily from nitro-derivatives of diazotised *p*-aminodiphenylamine [91]:



where $n = 0, 1, 2, 3$.

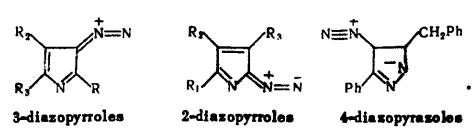
Morgan notes that the reaction rate and the stability of the *p*-iminoquinone diazide formed increase with increasing acidity of the substituent on the amino-nitrogen [91]:



Thus, trinitro-derivatives are obtained by adding sodium acetate to a hydrochloric acid solution, but the separation of a dinitro-derivative requires the addition of a more alkaline agent, such as potassium hydrogen carbonate, to the diazo-solution, and mononitro-derivatives are obtained from the diazo-solution only by adding ammonium hydroxide.

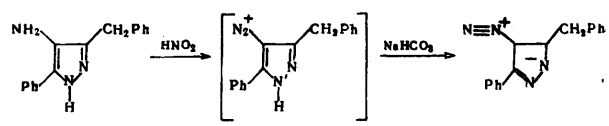
p-Iminoquinone diazides are also obtained from carbazole-3-diazonium chloride [92].

The following heterocyclic diazo-compounds may also be regarded as diazo-imines [93-95]:

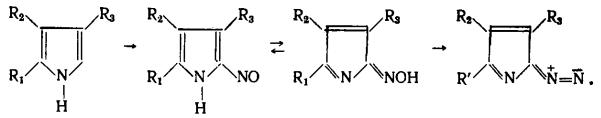


3-diazopyrroles 2-diazopyrroles 4-diazopyrazoles

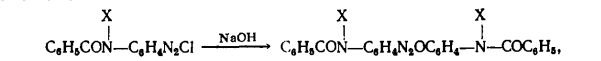
These compounds may be prepared by the usual diazotisation of the corresponding amine and neutralisation of the solution obtained [93,96]:



Tedder's method may also be used: in this the diazo-group is introduced into the ring with the aid of nitrous acid[94,95]:

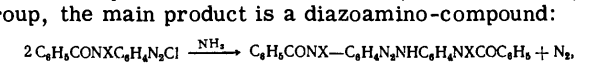


For a long time attempts to prepare *p*-iminoquinone diazides from *N*-formyl-, *N*-acetyl-, and *N*-benzoyl--amino-substituted diazonium salts were not successful. Morgan and coworkers showed that in these instances the use of ordinary alkaline agents leads to some unexpected results[97]. When the diazo-solutions of *N*-benzoyl-1,4--phenylenediamine and *N*-benzoyl-1,4-naphthylenediamine are treated with sodium acetate no precipitate is formed, but treatment with cold concentrated solutions of potassium hydrogen carbonate and sodium nitrite gives yellow crystalline precipitates, which Morgan regarded as aryldiazonium hydrogen carbonate and nitrite[97]. The action of alkali on *p*-*N*-benzoylaminophenyldiazonium chloride gives a different result: Morgan considers the main reaction product to be a diazo-oxide[98]:



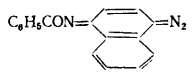
where X = H, CH_3, C_2H_5.

According to Morgan and coworkers, the action of ammonia depends on the substituent X; if X is an alkyl group, the main product is a diazoamino-compound:



if X = H, a mixture of diazo-oxide and diazoamino-compound is obtained. It has been shown that the action of a cold concentrated solution of potassium hydrogen carbonate, a cold solution of ammonium hydroxide, or a 0.1 *N* solution of sodium hydroxide on an aqueous solution of *p*-*N*-benzoylaminophenyldiazonium chloride at 0–4° leads to the formation of a yellow precipitate consisting of a mixture of diazonium chloride and the corresponding *p*-iminoquinone diazide, but the pure *p*-iminoquinone diazide *p*-$C_6H_5CONC_6H_4N_2$ could not be obtained in this way[99].

The action of alkali on the diazo-solution of *p*-*N*-benzo-amino-1,4-naphthylenediamine leads to the separation of a yellowish brown product, which Morgan regarded as the nitrosoamine $C_6H_5CONHC_{10}H_6NHNO$.[100] Later Dimrot and coworkers[101] showed that the *p*-iminoquinone diazide



is in fact formed, and not the nitrosoamine.

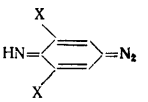
The preparation of *p*-iminoquinone diazides from *p*-*N*-acetyl and *p*-*N*-formyl-aminophenyldiazonium chlorides is still more difficult. Morgan and coworkers tried the effect of various alkaline agents ($KHCO_3$, $NaNO_2$, CH_3COONa, NH_4OH) on these diazonium chlorides[97]. No precipitate was obtained with potassium hydrogen carbonate or sodium nitrite; with sodium acetate the diazoamino--compound $R'CONHC_6H_4N_2NHC_6H_4NHCOR'$ was precipitated; and with ammonium hydroxide a compound was formed the analysis of which indicated that it was most likely a nitrosoamine.

Thus, the *p*-iminoquinone diazides $RNC_6H_4N_2$ (where R = HC(=O)–, CH_3C(=O)–, or C_6H_5C(=O)–) cannot be prepared by the usual method, that is, by the action of various alkaline agents on diazonium chlorides.

Morgan and coworkers[89,102] proposed another method of preparing *p*-iminoquinone diazides, consisting in the direct diazotisation of the amine $R'CONHC_6H_4NH_2$, where R' = H, CH_3, C_6H_5, with dinitrogen trioxide in a solution of dry acetone. The *p*-iminoquinone diazides obtained in this way are described as unstable compounds that cannot be purified, because they become more contaminated on recrystallisation; they are pale yellow, while all quinone diazides and *p*-iminoquinone diazides have a bright yellow, orange, or red colour.

Later it was shown[99] that the action of dinitrogen trioxide on *p*-*N*-acetyl- and *p*-*N*-benzoyl-*p*-phenylenediamines leads to the formation of the corresponding aryldiazonium nitrate and not to iminoquinone diazides.

The unsubstituted *p*-iminoquinone diazide $HNC_6H_4N_2$ could not be obtained at all. The ring-substituted *p*-iminoquinone diazides

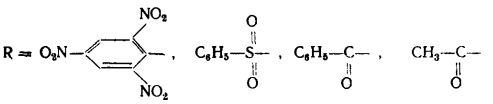


were obtained by the diazotisation of the corresponding amines with dinitrogen trioxide[102]. However, this work requires confirmation.

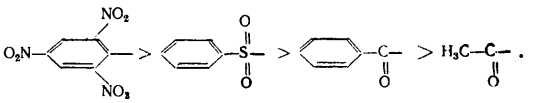
Thus, iminoquinone diazides (imidoquinone diazides) are only formed from *N*-substituted *p*-aminophenyldiazonium salts $RNHC_6H_4N_2^+X^-$; the reaction proceeds more readily as the electronegativity of the substituent R increases, and the ease of formation increases with the molecular weight of the *p*-iminoquinone diazide. The stability of the *p*-iminoquinone diazides increases in the same order. This explains why the *p*-iminoquinone diazides $RCON{:}C_6H_4{:}N_2$, where R = CH_3, C_6H_5, could not be obtained for a long time and why *p*-iminoquinone diazide itself

has not been prepared.

Ultraviolet and infrared spectroscopy have been used successfully to investigate the conversion of the diazonium chlorides $RNHC_6H_4N_2Cl$, where



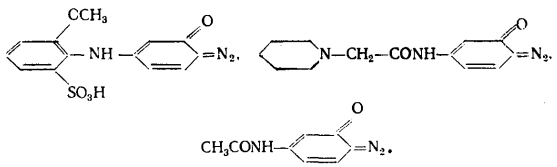
into the corresponding *p*-iminoquinone diazides in buffered solutions[99]. The two latter *p*-iminoquinone diazides decompose very rapidly in light at ordinary temperature. It has been shown that this conversion is an acid–diazo-cation dissociation. The strength of the acid $RNHC_6H_4N_2^+$ decreases in the following order according to the substituent R:



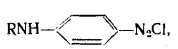
Thus, *p*-*N*-picrylaminophenyldiazonium chloride is instantly converted into the *p*-iminoquinone diazide even by dissolution in water, but an appreciable quantity of *p*-iminoquinone diazide is formed from *p*-*N*-acetylamino-phenyldiazonium chloride only in alkaline solutions of pH 9 or higher.

Para- and *ortho*-hydroxyphenyldiazonium chlorides are stronger acids, and they therefore form quinone diazides

more readily; this is due to the greater acidity of the hydroxyl group. Thus, diazonium salts with both OH– and RNH– groups in the ring form quinone azides [103,104], but not *p*-iminoquinone diazides, for example:



The special properties of hydroxy- or amino-substituted diazonium salts whereby they form quinone diazides and *p*-iminoquinone diazides when treated with alkaline agents is due, on the one hand, to the presence in the molecule of the hydroxy- or amino-group, which can eliminate a proton under certain conditions, and, on the other hand, to the presence of an extremely strong electronegative diazonium group, which confers acidity on the hydroxy- or amino-group in the *ortho*- or *para*-position. In the diazonium chloride



an electron-acceptor substituent R is also needed to ensure the elimination of a proton from the amino-group.

III. PROPERTIES OF QUINONE DIAZIDES AND *p*-IMINOQUINONE DIAZIDES

A. Physical Properties

Quinone diazides and *p*-iminoquinone diazides are coloured crystalline compounds, with colours varying from yellow to red.

Their behaviour with solvents greatly depends on their structure. Thus, *o*-quinone diazides are always more soluble than the *para*-isomers. Unsubstituted *o*- and *p*-benzoquinone diazides, their methyl and methoxy--derivatives, *p*-*N*-acet- and *p*-*N*-benziminoquinone diazides are very soluble. Arylsulphonyliminoquinone diazides are moderately or even poorly soluble in organic solvents and water. Some *p*-iminoquinone diazides are readily soluble in *p*-toluidine [86], but depression of the freezing point indicates that they form addition products with the solvent. The presence of a large number of condensed benzene rings in quinone diazides and *p*-iminoquinone diazides reduces the solubility of these compounds in water and increases the solubility in organic solvents. Thus, 1,2- and 2,1-naphthoquinone diazides are easily crystallised from aqueous solution [7,13], but are readily soluble in organic solvents. The introduction of negative substituents into quinone diazides reduces their solubility in both polar and non-polar solvents.

Some diazides contain water of crystallisation [10,24,105]. Hantzsch and Davidson studied a number of simple quinone diazides by the cryoscopic method and showed that they are not associated in solution [10].

All quinone diazides and *p*-iminoquinone diazides are sensitive to heat, and nitro-derivatives explode when heated in the dry state. The decomposition temperature largely depends on the rate of heating [106]. The thermal stability increases with the number of negative substituents in the nucleus.

Photosensitivity is a specific property of quinone diazides and *p*-iminoquinone diazides, the latter being the more sensitive to light. The use of these compounds in the printing industry is based on this property. *o*-Quinone diazides are more photosensitive than the *para*-isomers, and naphthalene derivatives are more sensitive than benzene derivatives.

A large amount of information on the use of diazides for the preparation of photosensitive compositions has been published in the patent literature [74-82] and has been reviewed by Saunders [1] and Dinaburg [107].

De Jonge and coworkers [108] determined quantum yields for the photolytic decomposition of quinone diazides irradiated in aqueous solution with light of wavelength 3500–4000 Å. They found that the quantum yield varies between 0.20 and 0.40, and they noted that, although the quantum yields are similar for all the compounds, variations in the photosensitivity of quinone diazides are due to differences in light-absorbing capacity. The more highly absorbing quinone diazides are more photosensitive. This also accounts for the higher photosensitivity of quinone diazides compared with diazonium salts; absorption curves of quinone diazides are displaced towards the long-wave side compared with the curves of diazonium salts.

The higher photosensitivity of *o*-quinone diazides compared with *para*-isomers may be explained in the same way.

Different physicochemical characteristics (spectra, dipole moments) are closely related to the structures of these compounds; for this reason, the relevant published information is considered in the section dealing with the structure of quinone diazides and iminoquinone diazides.

B. Chemical Properties

1. Diazide–diazonium acid–base equilibrium. It is characteristic of quinone diazides and *p*-iminoquinone diazides that they are converted into diazonium salts by the action of acids. Using ultraviolet spectroscopy, Kazitsyna and coworkers [99,109,110] made a detailed study of this transition as applied to unsubstituted, bromo-substituted and nitro-substituted *ortho*- and *para*--benzoquinone diazides, and the *p*-iminoquinone diazides $RNC_6H_4N_2$, where R = C_6H_5CO, CH_3CO, $C_6H_5SO_2$, or $(NO_2)_3C_6H_2$. The absorption curves obtained for *o*-benzoquinone diazides and *p*-benzenesulphonyliminoquinone diazides (Figs. 1 and 2) in various acidity regions have isobestic points, which indicates that only two forms (diazonium and diazide) occur in solution [110,111]. A similar picture is observed with substituted quinone diazides [110,112]. Therefore, the diazonium-cation–quinone diazide (*p*-iminoquinone diazide) change is an acid–base equilibrium.

Thus, quinone diazides and *p*-iminoquinone diazides are bases. These bases may differ greatly in strength. The *p*-iminoquinone diazides *p*-$CH_3CONC_6H_4N_2$ and *p*-C_6H_5-$.CONC_6H_4N_2$ are fairly strong bases; they are protonated, that is, converted into the corresponding diazonium cations, even in neutral or weakly alkaline solution [99]. Unsubstituted *para*- and *ortho*-quinone diazides and the *p*-iminoquinone diazides *p*-$C_6H_5SO_2NC_6H_4N_2$ are weak bases, and are protonated in acid solution, but within the limits of the pH acidity scale [109-111]. Bromo- and nitro-derivatives of quinone diazides, as weak bases, are only protonated in

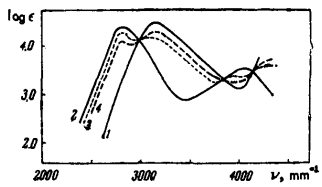


Fig. 1. Electronic absorption spectra of *p*-hydroxyphenyldiazonium chloride: 1) in 0.1 *N* HCl; 2) in water; 3) in 4×10^{-4} *N* HCl; 5) in 5×10^{-4} *N* HCl.

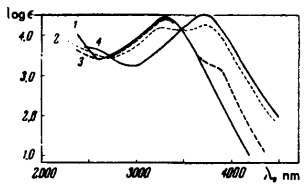
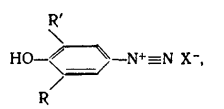


Fig. 2. Electronic absorption spectra of *p*-sulphonylaminophenyldiazonium chloride in buffer solutions. pH: 1) 1.1; 2) 3.5; 3) 2; 4) 4.8.

concentrated acids[66,110]. Ershov and Nikiforov made a spectrophotometric study of the conversion of *p*-quinone diazides with alkyl substituents in the *ortho*-position to the oxygen atom into the corresponding hydroxyphenyldiazonium salts[112]:



where R = R′ = H; R = R′ = CH_3; R = R′ = $CH(CH_3)_2$; R = = R′ = $C(CH_3)_3$; R = CH_3 and R′ = $C(CH_3)_3$, and found values for the logarithms of the equilibrium constants for this reaction. Their results show that quinone diazides with more branched alkyl substituents are weaker bases. The stability of the quinone diazide or *p*-iminoquinone diazide is inversely proportional to its basic strength.

Since diazides exist in aqueous solutions of different acidity in equilibrium with the diazonium form, it is sometimes difficult to decide whether the diazide or the diazonium form take part in the reaction. Authors of various papers on quinone diazides do not generally consider this aspect of the problem; for this reason, where possible, the form taking part in the reaction will be noted in the discussion on chemical properties.

2. Reactions in which nitrogen is retained. Both atoms are retained in many reactions of diazides and diazonium salts. Thus, with cyanides or sulphites quinone diazides form hydroxyaryl-diazocyanides or -diazosulphonates[10,43,66]. Like sulphurous acid, arylsulphonic acids react with quinone diazides to form sulphoazophenols[57,58]. As mentioned above, the same compounds are obtained by the action of arylsulphonyl hydrazides on quinones[56].

It has been reported that quinone diazides and their corresponding diazonium salts do not form perhalogen compounds[10,66].

Concentrated sulphuric acid sulphonates diazides of the naphthalene series[72], nitric acid nitrates them[72], and bromine brominates them[68]; in these reactions the substituent enters the 6-position. Diazides of the benzene series are brominated by bromine water[66].

In acid solutions of metal chlorides, quinone diazides form double salts, metal hydroxyaryldiazonium halides[10,66,113].

Hantzsch and Davidson[10], showed that, in the absence of acid, *p*-hydroxyphenyldiazonium salts form compounds of the type $HOC_6H_4N_2X.OC_6H_4N_2.MN_n$ with $CdCl_2$, CdI_2, and $HgCl_2$, but the action of cadmium iodide on quinone diazide leads to the formation of the compound $C_6H_4N_2O.CdI_2$. They put forward no hypotheses as to the structure of these compounds.

Kazitsyna and coworkers[113] made a detailed study of the reaction of *o*- and *p*-benzoquinone diazides with $ZnCl_2$, $CoCl_2$, $HgCl_2$, and $NaBF_4$. In aqueous and methanol solutions, finely crystalline, coloured compounds are formed, for which the following formula was proposed on the basis of elemental and infrared analysis:

$$[(HOC_6H_4N_2)_m\ OC_6H_4N_2]^{+m}\ [MCl_{n+m}]^{-m},$$
(II)

$m = 1$ with BF_4^-; $m = 2$ with $ZnCl_4^{2-}$, $CoCl_4^{2-}$.

The infrared spectra (ν_{CN_2} frequencies) indicates that there is some interaction between the quinone diazide molecule and the hydroxyphenyldiazonium cation.

A study of the reaction conditions showed that a weakly acid medium produced by partial hydrolysis of the salt is necessary for the formation of salts of this kind; the presence of this medium leads to quinone diazide–diazonium--cation equilibrium. Because of this property of quinone diazides, compounds of type (I) are obtained by the action of metal halides on both hydroxyphenyldiazonium salts and quinone diazides. When the acidity of the medium is increased, quinone diazides react with the metal halides to form ordinary hydroxyphenyldiazonium metal-halide salts.

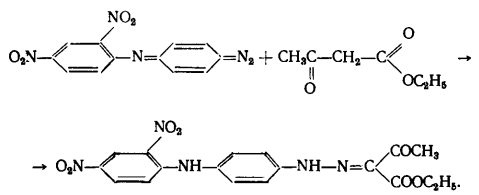
Mercury(II) chloride reacts with *o*- and *p*-benzoquinone diazides to form simple addition products of the composition $OC_6H_4N_2.HgCl_2$; Hantzsch found that mercury(II) iodide reacts in the same way.

The azo-coupling reaction of quinone diazides is of great importance, being widely used in industry for the synthesis of hydroxyazo-dyes, which form stable lakes with metal cations. Azo-coupling is also often used for the quantitative determination or identification of quinone diazides[51-54]. Diazides may be coupled in weakly acid or alkaline solution. The reaction conditions and characteristics determined with different compounds indicate that the compounds are capable of coupling in the diazide as well as in the diazonium form. The azo-coupling of diazides in acid solution is described in many patents[1]. In industry, hydroxyaryldiazonium salts are not separated in the dry state, but azo-coupling is carried out directly in solutions obtained after diazotisation, an alkaline solution of the azo-component being added.

Although no quantitative study has been made of the relation between the rate of azo-coupling and the nature of the substituent in quinone diazides, a number of rules governing the reaction may be noted. When the molecule contains a large number of condensed benzene rings, the tendency to form diazides increases, and these compounds couple less readily than simpler compounds, which are

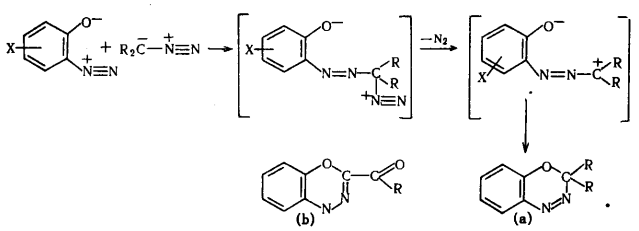
capable of being more easily converted into hydroxyaryldiazonium salts. *o*-Quinone diazides, which are formed more easily than *para*-compounds, also couple less readily than the *para*-isomers [36,38,54]. The introduction of negative substituents into the diazide nucleus leads to an increase in the positive charge on the diazo-group and significantly increases the tendency of the diazides to undergo azo-coupling [114]. Thus, Bamberger showed that unsubstituted 1,2- and 2,1-naphthoquinone diazides in alkaline solutions couple very slowly and only with active components [43,44]. Introduction of bromine or the cyano-group into the nucleus leads to more active coupling [20,68].

p-Iminoquinone diazides are also capable of undergoing the azo-coupling reaction. These compounds couple best with phenols, 2-naphthol, and resorcinol in dry pyridine [86]. Coupling occurs only with the most reactive amines: aniline and its homologues do not couple, but the reaction is quantitative with naphthylamines and toluene-2,4-diamine [86,115]. As Simonov showed [116], *p*-iminoquinone diazides couple with aliphatic and heterocyclic enols (ethyl acetoacetate, phenylmethylpyrazolone, etc.). The reaction proceeds readily at 20–30° in acetone solution:



The products are identical with those formed by the reaction of diazonium salts with enols.

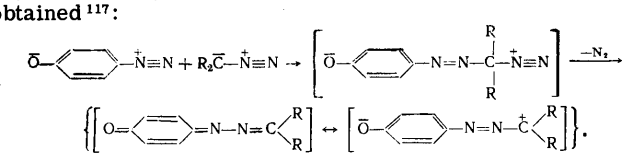
Huisgen and coworkers discovered the azo-coupling reaction of diazonium salts with aliphatic diazo-compounds [117]. These workers also coupled aliphatic diazo--compounds with quinone diazides [114]:



They noted that diazides have a much lower tendency to couple than ordinary aromatic diazonium salts; the introduction of negative substituents into diazides facilitates this reaction. The final products of coupling are derivatives of benzohydrooxadiazines (a). 1,2- and 2,1--naphthoquinone diazides do not undergo the coupling reaction.

If *o*-quinone diazides are coupled with diazo-carbonyl compounds, cyclic azoketones (b) are obtained as final products.

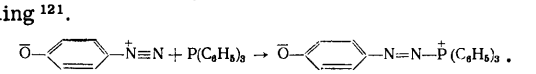
p-Quinone diazides may also react with aliphatic diazo--hydrocarbons, but substituted quinone azines are then obtained [117]:



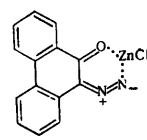
p-Quinone diazides do not react with diazo-carbonyl compounds.

Karlinskaya and Khromov-Borisov found that diazides of the pyrimidine series with a methyl group adjacent to the diazo-group are capable of intramolecular azo-coupling with the formation of indazole derivatives [118]. This reaction, of course, also occurs with diazonium compounds of the benzene series, while *o*-toluenediazonium salts form benzindazole derivatives [119].

Quinone diazides may also react with other nucleophilic compounds. Staudinger and Lüscher showed that quinone diazides, like aliphatic diazo-ketones, couple with triphenylphosphine to form quinonetriphenylphosphazines [120]. Reid and Appel made a detailed study of this reaction, and they noted that it is subject to the same rules as azo--coupling [121].



The *para*-compounds give a higher yield of phosphazines than the *ortho*-compounds, and the reaction is promoted by substituents that increase the positive charge of the diazo--group. Unsubstituted quinone diazides with condensed benzene rings undergo this reaction with difficulty. These compounds react more readily if a solution of quinone diazide and a Lewis acid are used. The authors consider that an intermediate complex of type (II) is formed, in which the Lewis acid increases the positive charge on the diazo-group:

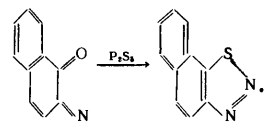


(II).

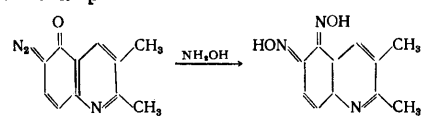
An increase in the positive charge on the diazo-group increases the tendency of quinone diazides to react with triphenylphosphine and it also increases the frequency of the stretching vibrations of the CN_2 group in the infrared absorption spectra of the diazides. It is therefore thought that the value of ν_{CN_2} may give an indication of the reactivity of a quinone diazide.

The reactions mentioned above occur with both diazides and diazonium salts, but some reactions have been described that are characteristic of diazides only.

Bamberger showed that when naphthoquinone diazide is treated with phosphorus pentasulphide, oxygen is replaced by sulphur and thiadiazole derivatives are formed by ring closure [43]:



It has been found that quinone diazides of the heterocyclic series react with hydroxylamine to give quinone dioximes as final products [122]:

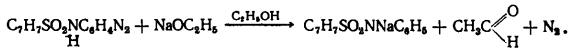


This reaction has not been further studied, but it may be supposed that it is applicable to many diazides, and might probably be a convenient method for synthesising otherwise inaccessible quinone dioximes.

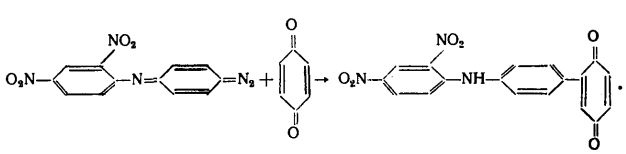
3. Reactions in which nitrogen is eliminated. In acid solutions diazides undergo all the reactions that are observed with solutions of diazonium salts

in general. Thus, in acid solutions of copper(I) chloride quinone diazides undergo the Sandmeyer reaction with the liberation of nitrogen and the formation of the corresponding chlorophenol derivative[24,34,123]. When quinone diazides are treated with potassium iodide or hydriodic acid, nitrogen is also liberated and iodophenols are formed[35,123]. When diazides are boiled in acid aqueous solution, the diazo-group is replaced by a hydroxyl group, but strong oxidation occurs and azo-dyes are also formed[43,66,124]. Reduction of the diazides with tin and hydrochloric acid gives the corresponding aminophenols with the liberation of ammonia[66]. Milder reducing agents, such as tin(I) chloride in hydrochloric or acetic acid, lead to the formation of hydroxyarylhydrazines[66,114,125]. When quinone diazides are boiled in alcoholic solution, the diazo-group is replaced by hydrogen, and the corresponding phenols are formed[30,31,126]; sometimes the reaction is carried out in the presence of alkalis or with the addition of metal powders[20,70]. This reaction was first studied in detail by Cameron[126], who established that replacement of the diazo-group by an alkoxyl group competes with replacement by hydrogen, and with alcohols higher than methanol the second reaction begins to predominate. Negative substituents in the nucleus facilitate the replacement of the diazo-group by hydrogen, and replacement occurs more readily in *ortho*- than in *para*-isomers. Hodgson and Bartwell[127] noted that negative substituents also accelerate the azo-coupling side-reaction, and the yield of reduction product therefore decreases in the order: $NO_2 < Cl < Br < I < SO_3H$. For the reduction, these workers used tin(I) chloride, or powders of aluminium, zinc, iron, or Devarda's alloy[70,126]. Horner and Dürckheimer successfully used hypophosphorous acid as a reducing agent in the presence of hydrochloric acid[65]. Replacement of the diazo-group by hydrogen is a reaction characteristic not only of quinone diazides, but also of various diazonium salts. Kornblum has published a review of the literature on this subject[128].

p-Iminoquinone diazides are reduced by sodium ethoxide, the diazo-group being replaced by hydrogen[86]:



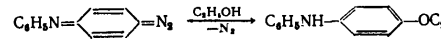
When *p*-iminoquinone diazides are heated with alkalis, resins are formed[83]. Like diazonium salts, *p*-iminoquinone diazides arylate quinones[116]:



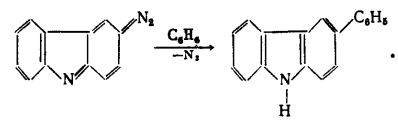
4. Photolytic and thermal decomposition of quinone diazides and *p*-iminoquinone diazides. Since many quinone diazides and *p*-iminoquinone diazides are used as photosensitive and explosive materials, the photochemical and thermal decomposition of these compounds has been intensively studied in recent years. It has long been known that hydroxydiazonium and *p*-aminophenyldiazonium compounds are more photosensitive than other diazonium salts[129]. However, the mechanism of the action of light on diazides has only been elucidated quite recently. Süs[130] and de Jonge and coworkers[131] began to study this question at the same time.

The study of the photochemical and thermal decomposition of these compounds led to the discovery of new methods of synthesising many compounds of different types that were difficult to obtain.

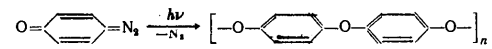
When *p*-quinone diazides and *p*-iminoquinone diazides are irradiated in alcoholic solution, monoalkyl ethers of aromatic *p*-dihydroxy-derivatives and *p*-aminophenols are obtained[8]:



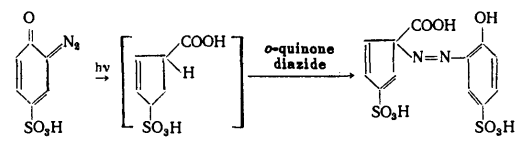
The photochemical decomposition of *p*-quinone diazides and *p*-iminoquinone diazides dissolved in aromatic hydrocarbons is used preparatively as a method of arylation and for the preparation of hydroxy- and amino-derivatives of these hydrocarbons, and also for the preparation of various heterocyclic compounds[8]:



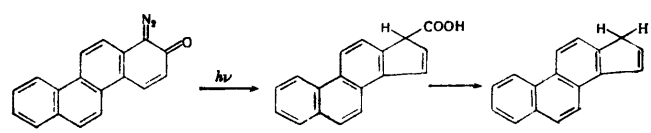
The photodecomposition or thermal decomposition of *p*-iminoquinone diazides and *p*-quinone diazides in the absence of water and polar organic solvents leads to the formation of thermostable polymers[8,132]:



Under the action of ultraviolet light the decomposition of *o*-quinone diazides proceeds quite differently. Süs who made a detailed study of this reaction, established that photolysis of *o*-quinone diazides is accompanied by ring contraction. Süs showed[130] that irradiation results in the formation of either a derivative of cyclopentadienecarboxylic acid, or the product of azo-coupling of this acid with the starting quinone diazide, the product depending on the structure of the latter:



Later, Süs and other workers studied the photolysis of *o*-quinone diazides of the naphthalene series[7,134], *o*-quinone diazides with condensed aromatic rings[7,10], and *o*-quinone diazides of the heterocyclic series[7,133,134]. In reviewing his papers on this subject, Süs[135,136] put forward some general rules governing the photolysis of *o*-quinone diazides and showed that this reaction can be used for the synthesis of new cyclic systems. For example, irradiation of chrysene-1,2-quinone 1-diazide enabled a compound with a steroid skeleton to be synthesised[7]:

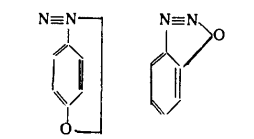


While the manuscript of this review was being prepared for the press, Dinaburg's monograph on photosensitive diazo-compounds and their applications appeared[107]; this gives a review of the literature on the photolytic decomposition of *p*- and *o*-quinone diazides and *o*-iminoquinone diazides. For this reason, we shall not consider these interesting reactions in detail here.

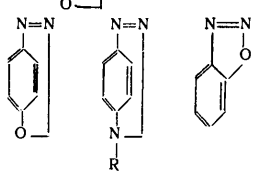
IV. STRUCTURE OF QUINONE DIAZIDES AND *p*-IMINOQUINONE DIAZIDES

The diazides are one of the classes of organic compounds the structure of which cannot be definitely established by chemical methods alone. The main conclusions as to the structure of these compounds have been drawn from the results of physicochemical investigations. We shall briefly consider this problem below and we shall analyse its present status in more detail. We shall first consider the structure of simple diazides, and then the structure of substituted diazides. We shall primarily consider material on the structure of the quinone diazides.

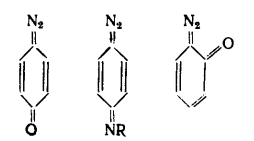
The following formulae have been proposed at different times for quinone diazides and *p*-iminoquinone diazides:



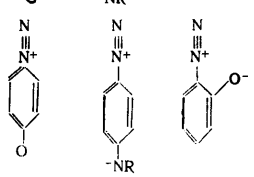
(I)



(II)



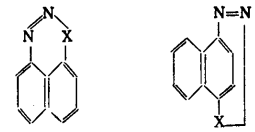
(III)



(IV)

Formula (I), containing quinquecovalent nitrogen, which was proposed by Bamberger [137], is incorrect according to modern interpretations. This formula was last used by Klemenc [124]. If Zsollinger's view [2] is accepted and the bridge bond is considered to be ionic, then this structure reduces to formula (IV).

For a long time a selection could not be made between the cyclic (II) and the quinoid (III) formulae to describe the structure of the quinone diazides and *p*-iminoquinone diazides. After the work of Morgan and coworkers [138,139], the cyclic formula (II), which had also been proposed by Bamberger [137], was considered almost up to the 1950's. Although there are now convincing proofs for the rejection of this formula, [9,13,14] some workers use it for *o*-diazides even today.[118] This is because the following facts favour the cyclic structure: (1) the yellow colour, which may be explained by the presence of the –N=N– group, as in coloured azo-compounds; (2) many properties, such as stability, azo-coupling, etc., have been associated with the presence of an easily cleaved oxydiazole ring; (3) finally, Morgan and coworkers reported (obviously in error) that diazo-oxides and diazoimides with similar properties are obtained from *peri*- and *para*-aminonaphthols and *peri*- and *para*-naphthylenediamines [138,139]. But since *peri*-derivatives cannot have a quinoid structure, both diazo-oxides and both diazoimides must have a cyclic structure:



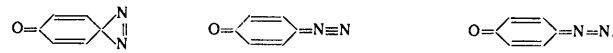
(where X = O or RN).

Using the analogy of the cyclic configuration of 1,4-diazoiminonaphthalene, Morgan proposed the cyclic formula (II) for the whole series of *p*-diazoimides, although he did not definitely reject the quinoid formula (III).

The following facts favour the quinoid structure for diazoimides and diazo-oxides: (1) colour and photosensitivity; (2) negative experiments on the preparation of *p*-diazoimides and *o*-diazo-oxides [74]; (3) differences in physical and chemical properties between *p*-diazoimides and *o*-diazoimides (the latter in fact have a cyclic structure); (4) it is difficult to suppose that the formation of *p*-diazo-oxides and *p*-diazoimides, which occurs readily (and sometimes instantaneously) in the cold, is associated with the closure of a seven-membered ring; (5) the ultraviolet and infrared spectra of the quinone diazides, which will be discussed below; (6) finally, Anderson and Roedel reported [13] that when they repeated Morgan's synthesis [140] they were unable to obtain the cyclic diazo-oxides he described from *peri*-aminonaphthol [13].

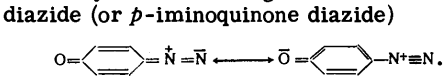
It will be seen that there is much more evidence in favour of the quinoid structure (III) and it has therefore been given preference over the others.

The quinoid structure, which is generally ascribed to Wolff [140], was first put forward without proofs by Bamberger [141] as one of the possible formulae of the quinone diazides; it could not be written unambiguously, because the structure of the diazonium group was not known. Later, following Wolff, this structure was accepted by Hantzsch [76,142] and other workers [9,13]. Bamberger [141] and Hantzsch [142] considered that the structure (IIIa) was the correct one. Bamberger [143] also proposed the formula (IIIb), which Angeli accepted [144]. In accordance with modern interpretations, the quinoid formula of the diazides is written in the form (IIIc):



(IIIa) (IIIb) (IIIc)

However, even the quinoid formula cannot exactly describe the structure of the quinone diazides and *p*-iminoquinone diazides. Recently, there has been an increasing tendency to accept the intra-ionic formula (IV), not as an independent formula, but as one of the extreme structures in a resonance hybrid describing the structure of the quinone diazide (or *p*-iminoquinone diazide)



(IV)

Sidgwick and coworkers were the first to put forward the idea of mesomerism of this type [145], and Modling and Burger represented quinone diazides in the same way [122]. Simonov [116] proposed mesomerism of ionic and quinonoid structures for iminoquinone diazides. Later, the mesomerism of these structures was used repeatedly to explain the properties of diazides [1,94,127].

It was characteristic of Hantzsch that as early as 1890 he noted that one formula alone was not sufficient to describe the properties of the diazides, and he thought that oscillation between the structures (I) and (III) was possible [10].

A. Structure and Physicochemical Properties of Quinone Diazides

As mentioned above, more precise determination of the structure of diazonium compounds became possible only with the development of physicochemical methods of investigation.

In 1945 Anderson and coworkers began the publication of papers in which they reported studies on the ultraviolet spectra and dipole moments of some quinone diazides of the benzene and naphthalene series; they compared their results with corresponding data for quinones and compounds containing triazole or thiodiazole rings [13,14]. They noted that the *o*- and *p*-quinone diazides have similar properties and their spectra are similar to the spectra of the corresponding quinones. However, the quinone diazides and cyclic thiodiazoles did not show similarities in their dipole moments and spectra. These workers concluded that the cyclic structure for quinone diazides is entirely ruled out, and they assigned a quinonoid structure to these compounds.

The results of dipole-moment measurements on six quinone diazides published by Anderson and coworkers (see Table 2) show that the *o*-quinone diazides are more "quinonoid" than the *para*-compounds [14]. The introduction of a nitro-group into the molecule increases the dipole moment.

Vaughan and Phillips studied the thermal stability of unsubstituted and nitro-substituted *o*- and *p*-quinone diazides, and showed that the *o*-quinone diazides are thermally no less stable than the *para*-isomers [106]. A nitro-group in the *ortho*- or *para*-position to the hydroxyl group stabilises the molecule, two nitro-groups have a greater effect, and a nitro-group in the *meta*-position has no effect. The results were regarded as being in agreement with the hypothesis that quinone diazides have a structure intermediate between the quinonoid and ionic structures.

TABLE 2. Dipole moments of quinone diazides

Compound	μ_H	μ_X	μ_I^*
3,5-Dibromobenzo-1,2-quinone 2-diazide	2.9	2.5	13.1
Naphtho-1,2-quinone 1-diazide	4.0	3.9	13.7
Naphtho-1,2-quinone 2-diazide	3.5	3.9	13.7
4-Nitronaphtho-1,2-quinone 1-diazide	4.6	2.8	16.2
1,4-Naphthoquinone diazide	4.2	1.6	27.4
p-Benzoquinone diazide	5.0	1.6	27.4

* μ_H dipole moment found experimentally; μ_X dipole moment calculated for the quinonoid form; μ_I dipole moment calculated for the ionic form.

On the bases of differences between ultraviolet absorption spectra of solutions of hydroxyphenyldiazonium sulphate in 5 *N* sulphuric acid, De Jonge and coworkers [146] concluded that the structure of *o*-benzoquinone diazides was intermediate between the quinonoid and ionic forms; they consider that in acid solutions the structure is close to that of benzene, since under these conditions, the quinonoid structure is energetically less favoured. In aqueous solutions the structure of the compound is close to the quinonoid form. These workers explain the different behaviour of *o*-hydroxyphenyldiazonium sulphate in neutral and acid aqueous solutions, and particularly the difference in ultraviolet absorption spectra and the different course of the photodecomposition reaction, by the hypotheses mentioned above. However, as mentioned above (see Section III.B.1), this is not a question of the quinonoid and benzenoid structure of *o*-benzoquinone diazide, but of the existence of an *o*-hydroxyphenyldiazonium cation in acid solutions and of *o*-benzoquinone diazide in aqueous solutions.

In recent years a large number of papers have appeared on the infrared absorption spectra of various quinone diazides. Intense absorption bands were always observed in the region of stretching vibrations of a triple bond and in the region of vibrations of the carbonyl group, which confirms the quinonoid structure, or in the opinion of a number of workers, the "mesomeric" structure of diazides. In the first paper of this type, published in 1954, the infrared spectra of seven quinone diazides were studied; the results are shown in Table 3.[147]

These results were compared with the frequency of the stretching vibrations of the CN_2(ν_{CN_2}) bond of phenyldiazonium tetrafluoroborate (ν_{CN_2} = 2296 cm^{-1}) and with the frequency of the stretching vibrations of the N–N ($\nu_{-N=N-}$) bond of benzo-1-thia-2,3-diazole ($\nu_{N=N}$ = 1542 cm^{-1}) and it was concluded that in quinone diazides the bond between the nitrogen atoms is intermediate between double and triple, and that the carbonyl group has the C=O structure.

Whetsel and coworkers [9] studied the infrared spectra of a number of diazonium salts, including diazonium compounds obtained from some aminophenols. They found the absorption bands in the region of diazo-group vibrations shown in Table 4.

To explain the lower values of ν_{CN_2} of quinone diazides compared with diazonium salts, the authors suggested that in the solid state the structure of quinone diazides is intermediate between the ionic and quinonoid forms.

TABLE 3. Infrared spectra of quinone diazides.

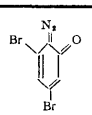
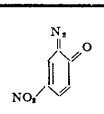
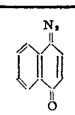
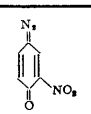
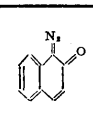
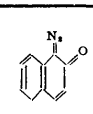
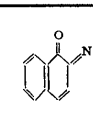
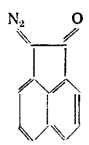
Diazide							
ν_{CN_2}, cm^{-1}	2110	2157	2014	2173	2017	2015	2148
ν_{CO}, cm^{-1}	1582	1562	1618	1618	1622	1642	1610

TABLE 4. Infrared spectra of diazo--compounds.

Diazo-compound from	ν_{CN_2}, cm^{-1}
m-Aminophenol tetrafluoroborate	2288
p-Aminophenol chloride	2237
p-Aminophenol diazide	2107
4-Nitro-2-aminophenol diazide	2183

In recent papers that contain information on the infrared spectra of quinone diazides, the authors either do not consider the relationship between spectra and structure at all[60,65,104,148,149], or they attempt to find if quinone diazide has a quinonoid, benzenoid, or mesomeric structure[150,151].

Reid and Appel[121] relate ν_{CN_2} with the reactivity of quinone diazides; they consider that the higher the value of ν_{CN_2}, the more vigorously the compound couples with triphenylphosphine. Thus, if $\nu_{CN_2} = 2125$ cm^{-1}, the compound does not undergo this reaction; if the value of ν_{CN_2} is 2125–2200 cm^{-1}, the compound couples very readily, and when $\nu_{CN_2} > 2200$ cm^{-1}, an anomalously fast reaction is observed. It is of interest that, on the basis of results obtained, these workers concluded that the quinone diazide (V) obtained from acenaphthoquinone is more an aliphatic diazoketone than a quinone diazide. This is in agreement with the conclusion based on a study of the infrared spectra of acenaphthoquinone.



(V)

All that has been said above on the structure of quinone diazides corresponding to aromatic hydrocarbons is also valid for diazides of the heterocyclic series. The spectra of these compounds show C=N̊=N̄ (or C–N̊≡N) and C=O stretching vibration bands[60,63], but the chemical properties of the compounds are the same as those of diazides of the aromatic series. Thus the similarity between the heterocyclic and aromatic diazides clearly shows that the former do not contain the oxydiazole ring[118], but have either a quinonoid structure[151], or, like uracil derivatives, the structure of a hydroxydiazonium compound[152].

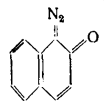
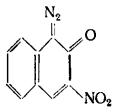
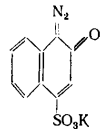
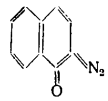
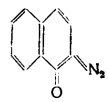
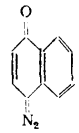
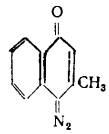
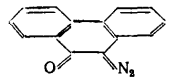
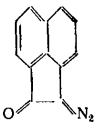
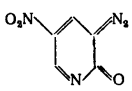
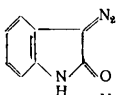
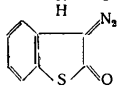
Table 5 gives information on the stretching vibrations of C=N̊=N̄ and C=O bonds of diazides. Not all results are of the same value, since they were obtained under different conditions and with different degrees of precision (NaCl, LiF prisms, differences in degree of purity of the compounds, etc.). This is the reason why some frequencies given by different workers for the same compounds do not coincide. Another reason for the discordance probably resides in peculiarities in the structure of the diazides — peculiarities that have not yet been studied. Diazides obtained under different conditions may have different crystal structures, or their crystals may sometimes contain solvent molecules. The results of elemental analyses are not always given for diazides. This probably explains why the same compound may show one ν_{CN_2} band, or this band may sometimes be split into two or more components. Nevertheless, for the sake of completeness, we included a large proportion of the published results in Table 5.

The spectra of quinone diazides have a number of characteristic features. An increase in the number of condensed benzene rings in the quinone diazide molecule reduces ν_{CN_2} and increases $\nu_{C=O}$ at the same time. The value of $\nu_{C=O}$ for diazides varies within the limits 1630–1570 cm^{-1}; the results obtained by Glowiak form the only exception to this rule[150]. The values of ν_{CN_2} vary within the limits 2200–2000 cm^{-1}; higher values are observed only with carboxylic acids; these diazides containing the carboxyl or sulpho-group will be considered below. The stretching vibration band of the C=N̊=N̄ bond in *o*-diazides is nearly always split into two components, but no splitting occurs with the *para*-isomer. This interesting phenomenon has not been explained, and no research worker has even considered it. As a rule, the value of ν_{CN_2} for diazides is increased by electronegative substituents and diminished by electropositive substituents. However, this relationship, on the basis of which a number of workers have drawn conclusions about the structure and reactivity of the quinone diazides, is not very pronounced, and examples may be found in Table 5 in which substituents have the opposite effect. No such relationship is observed with regard to the effect of substituents on the

TABLE 5. Values of ν_{CN_2} and ν_{CO} for quinone diazides.

Substituents	ν_{CN_2}	ν_{CO}	References
ortho-quinone diazides			
Unsubstituted	2175, 2140	1620	65
»	2134, 2168	1626	162
5-OCH_3	2128	1620	65
3-OCH_3, 6-OCH_3	2135, 2087	1613	65
5-OCH_3·C_6H_5	2150	1620	65
5-CH_3	2175, 2130	1613	65
4,5-$(CH_3)_2$	2170, 2120	1625	65
4,5-$(CH_2)_3$	2180, 2135	1637	63
4,5-$(CH_2)_5$	2150, 2100	1625	132
5-$C(CH_3)_3$	2182, 2160	1618	65
3,5-$[C(CH_3)_3]_2$	2135, 2124	1625	65
4,6-$[C(CH_3)_3]_2$	2120	1622	143
4,6-$[C(CH_3)_3]_2$	2170	1622	63
4-$CHC_6H_5C_6H_5$	2200, 2130	1630	132
4-C_6H_5	2100	1620	142
4-$NHCOCH_3$	2200, 2150	1640, 1630	132
4-$COCH_3$	2150	1700, 1630 w.	104
4-COC_6H_5	2170	1610, 1580	104
5-Cl	2205, 2158	1613	65
6-Cl	2195, 2158	1610	65
4-Cl, 5-Cl	2160	1613	65
3-Br, 5-Br	2110	1582	147
4-Br, 6-Br	2152s.	—	162
4-COOH	2215	—	9
4-NO_2	2157	1562	147
4-NO_2	2183, 2150	—	9
4-NO_2, 6-COOH	2223	1760, 1616	150
6-NO_2, 4-COOH	2235	—	121
4,6-$(NO_2)_2$	2225	—	121
	2190	1666	150
4,6-$(NO_2)_2$-3-OH	2132	1664	150
4,6-$(NO_2)_2$, 6-COOH	2190, 2207	1739	150
para-quinone diazides			
Unsubstituted	2109	—	9
»	2080	—	16
»	2110s.	1578	162
Unsubstituted.$4H_2O$	2080		16
Ditto	2125, 2135s.		162
2,6-$(CH_3)_2$	2090	1615	63
2,6-$(CH_3)_2$	2060	1600	159
2,6-$(CH_3)_2$	2070	—	16
2,6-$(CH_3)_2$·$4H_2O$	2070	—	16
3,6-$(CH_3)_2$	2105	1610	63
2-CH_3, 6-COOH	2225	—	121
2-Cl, 6-Cl	2140	—	121
2-Br, 6-Br	2122s., 2144s.	—	162
2-NO_2, 6-COOH	2225	—	121
2,6-$(NO_2)_2$, 3-CH_3	2207	1653	150
5,6-Br_2	2140	1615	63
5-Cl, 6-Cl	2175	1610	63
5-F, 6-F	2190	1605	63

TABLE 5 (contd.)

Compounds	ν_{CN_2}	ν_{CO}	References
Quinone diazides of the naphthalene series			
	2132w., 2096	1621	148
ditto	2110	—	54
»	2017	1622	147
	2015	1642	147
	2089s., 2109s.	—	162
	2155w., 2114	1621	148
ditto	2090	—	54
»	2148	1610, 1618	147
	2150, 2180	—	121
	2014	1618	147
	2090	1625	63
Quinone diazides with condensed benzene nuclei			
	2066	1631	60
ditto	2100, 2125	—	121
Chrysene-5,6-quinone 6-diazide	2090	—	121
Fluoranthene-2,3-quinone diazide	2095	1635	63
	2070	1667	60
Quinone diazides of the heterocyclic series			
	2024	1716	151
	2092	1704	60
	2095	1625	63

value of $\nu_{C=O}$; the frequency varies very little and substituents of the same type may increase it or reduce it. The value of ν_{CN_2} is always higher for *ortho*-isomers than for the corresponding *para*-compounds. The integral intensity of the absorption band of the CN_2 bond in *o*-benzoquinone diazide is half that of the band for the bond in the *para*-isomers [153].

B. Structure of Substituted Quinone Diazides

The study of infrared spectra, especially in the 2000–2300 cm^{-1} region, that is, in the absorption region of $C=\overset{+}{N}=\bar{N}$ and $C-\overset{+}{N}\equiv N$ groups, is very useful in the determination of the structure of quinone diazides. But when this method is used, other physical and chemical properties of the quinone diazides and the corresponding diazonium salts must be taken into account.

In examination of the structure of the quinone diazides, it is generally assumed that diazides with high values ν_{CN_2} have a structure closer to the benzenoid form, and those with low values have a structure closer to the quinonoid form. However, examination of the data in Table 5 shows that one value of ν_{CN_2} alone is not sufficient to enable a decision to be made as to whether a compound is more or less benzenoid (or quinonoid). For example, Table 5 shows that the value of ν_{CN_2} is higher for *o*-diazides than for *p*-diazides, but chemical properties and dipole-moment measurements show that *o*-quinone diazides are more quinonoid than *p*-diazides [14]. Moreover, workers studying the structure of quinone diazides have not compared values of ν_{CN_2} obtained for quinone diazides with values for the corresponding hydroxyaryldiazonium salts (known to have a benzenoid structure), but have limited themselves to comparisons within the diazides. But experimental results show that for each quinone diazide there is a corresponding hydroxyaryldiazonium salt; the values of ν_{CN_2} in the spectra of the diazonium salts are higher than the values for the corresponding quinone diazides by 100–150 cm^{-1} (Table 6).

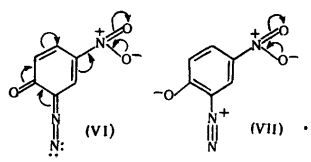
Thus, those diazides with high values of ν_{CN_2}, which are considered by many workers to exist in the benzene form, must have corresponding diazonium salts with known benzene structures and with still higher values of ν_{CN_2}. For example, ν_{CN_2} = 2190 cm^{-1} for 4,6-dinitrobenzo-1,2-quinone 2-diazide [150]. The corresponding hydroxyphenyldiazonium cation containing two nitro-groups, if it exists, must have a ν_{CN_2} of about 2300 cm^{-1}.[154] Therefore, higher values of ν_{CN_2} for substituted quinone diazides do not indicate that these compounds have a more benzenoid structure, since the corresponding benzene form (hydroxyphenyldiazonium salt) has a still higher value of ν_{CN_2} compared with these quinone diazides.

TABLE 6*.

Compound	ν_{CN_2} of quinone diazide			ν_{CN_2} of diazonium chloride*
p-Benzoquinone diazide	2107 s.	—	2278 w.	2251 m.
4,6-Dibromobenzo-1,2-quinone 2-diazide	2122 s.	2144 s.	2260 w.	2248 m.
o-Quinone diazide	2107 s.	2132 s.	2063—2169s.	2247 m.
1-Diazo-2-hydroxy naphthalene 4-sulphonic acid	2089 s. (potassium salt)	2109 s.	2230 w.t	2229 (internal salt)

* s. strong band; m. band of moderate intensity; w. weak band.

The increase in ν_{CN_2} observed when negative substituents are introduced into the quinone diazide occurs, because these substituents, acting on the diazo-group through the ring, withdraw electrons from this group, in the same way as the presence of a nitro-group in the ring of the nitrophenyldiazonium cation leads to a reduction in the electron density of the diazonium group. Although the diazo-group of the quinone diazide is somewhat similar in type to the diazonium group, the effect of substituted nitro-groups is to decrease the electron density of the oxygen of the C=O group, and not to increase it, as would be required for the intra-ionic benzene structure (VII)

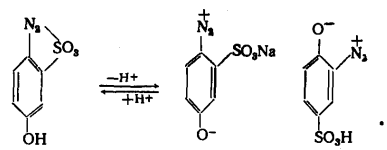


(VI) (VII)

Thus, quinone diazides with electronegative substituents, in contrast to the corresponding diazonium cations, do not have a benzenoid structure but the structure (VI), which is characteristic of unsubstituted quinone diazides; in this structure electrons are somewhat displaced towards the electronegative substituent.

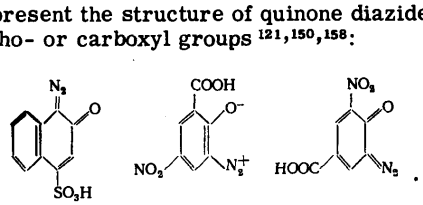
Compounds containing a carboxylic or sulphonic group occupy a special place in the hydroxyaryldiazonium series. In these compounds the diazonium group may interact with the acid group to form an internal diazosulphonate, and with the hydroxyl group to form a quinone diazide. Although the structure of these compounds has been under discussion for 50 years, the question has still not been finally cleared up.

Morgan and Tomlins [155], Battegay and Schmidt [156], and Schmidt and Maier [157] have discussed the structure of hydroxyaryldiazosulphonic acids. Some information on this question has been systematised in the book by Saunders, in which the literature up to 1949 is examined [1]. Saunders noted that in acid solutions these compounds are colourless and appear to be internal diazosulphonates (VIII), but in alkaline solutions they are yellow and probably have the structure (IX). Saunders ascribed the structure (X) to some quinone diazides that are coloured in acid solution, for example, 4-sulphobenzo-1,2-quinone 2-diazide:



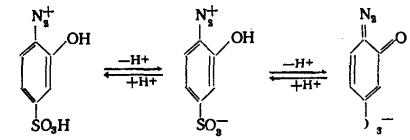
(VIII) (IX) (X)

At present a number of workers use formulae (XI)–(XIII) to represent the structure of quinone diazides containing sulpho- or carboxyl groups [121,150,158]:



(XI) (XII) (XIII)

In any examination of the structure of these compounds, it should be noted that hydroxyphenyldiazonium cations containing sulpho- or carboxyl groups are dibasic acids:



(XIV) (XV) (XVI)

The first acidity constant, corresponding to dissociation of the sulpho-group, is much greater than the second constant, corresponding to the dissociation of the hydroxyl group (it is well known that sulphonic and carboxylic acids are more acidic than phenols). Therefore, in acid solutions, in which dissociation of the hydroxyl group is suppressed, these compounds exist as the internal diazonium salt (XV). In neutral and weakly acid solutions, in which dissociation of the hydroxyl group is possible, the compound must exist as an equilibrium mixture of form (XV) and the diazide form (XVI). Finally, in alkaline solutions these compounds have the quinonoid structure (XVI). Thus, the solid compound obtained from acid solutions is the internal diazonium salt (XV). From neutral solutions that form separates which has the lowest solubility under the given conditions. Obviously, this will be form (XV), since it is known that internal diazonium salts of sulphonic acids are poorly soluble in water, but quinone diazides with an ionised sulpho-group should be much more soluble. From alkaline solutions the quinonoid form of the compounds will separate as the metallic salt of the acid, for example:

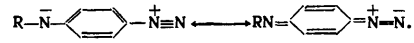
$$O{=}C_6H_3{=}N_2\ (SO_3Na)$$

(XVII).

Thus, these compounds never exist in the form of quinone diazide with an un-ionised sulphonic of carboxylic group — structures (X), (XI), and (XIII).

C. Structure of *p*-Iminoquinone Diazides (*p*-Imidoquinone Diazides)

As early as 1940, Simonov [116], who examined the chemical properties of *p*-iminoquinone diazides, rejected the cyclic formula proposed by Morgan [139] and proposed that the structure of these compounds cannot be generally represented by a single formula, but rather by the superposition of ionic and quinonoid structures:



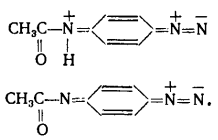
He emphasised that these structures were in a mesomeric and not a tautomeric relationship.

The state of the compound will be determined by the predominance of one structure or the other, according to the strength of the competing effects of the diazonium group and the substituent R. If the substituent is a weak electron acceptor (R = $CH_3-\overset{O}{\overset{\|}{C}}-$, $C_6H_5-\overset{O}{\overset{\|}{C}}-$, C_6H_5-), equilibrium is displaced towards the formation of the quinonoid structure, but if the substituent is a strong electron acceptor, as when R = $ArSO_2-$, $(NO_2)_3C_6H_2-$, etc., then the dipolar-ion structure predominates; in other words, the *p*-diazoimine (*p*-diazoimide) structure is regarded as the internal diazonium salt.

TABLE 7.

Substituent	Diazonium chlorides: ultraviolet spectrum λ_{max}, nm	Diazonium chlorides: ultraviolet spectrum log ϵ	Diazonium chlorides: infrared spectrum ν_{CN_2}, cm^{-1}	Diazonium chlorides: colour	p-Iminoquinone diazides: pH region in which the two forms are in equilibrium in solution	p-Iminoquinone diazides: ultraviolet spectrum λ_{max}, nm	p-Iminoquinone diazides: ultraviolet spectrum log ϵ	p-Iminoquinone diazides: infrared spectrum ν_{CN_2}, cm^{-1}	p-Iminoquinone diazides: colour	Literature reference
$C_6H_5SO_2NH$	327	4.41	2259	colourless	1.1—4.8	372	4.56	2181	yellow	111
CH_3CONH	335	4.49	2250	colourless	8.2—12	395	4, ...		yellow	99
C_6H_5CONH	342	4.52	2255	colourless	7.5—11.8	405	4.48	2150	yellow	99
C_6H_5NH	376	4.56	2244					2208		
			—	—	—	394	4.52	—	—	160
$(NO_2)_2C_6H_3NH$	—	—	2236	yellow	—	—	—	2112	red	99
								2090		

The hypotheses and conclusions of Simonov were not confirmed by studies of the physicochemical properties of *p*-iminoquinone diazides. Anderson and coworkers used ultraviolet and visible absorption spectra to establish the structure of the *p*-diazoimines [160,161]. According to their results, the ultraviolet spectra of solutions of *p*-diazoimines are identical with those of the corresponding diazonium chlorides. These workers were not surprised at this finding, because they considered that both the diazonium cation and the *p*-iminoquinone diazide have the quinonoid structure:

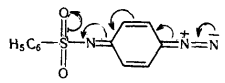


But the properties of the *p*-iminoquinone diazides differ from those of the corresponding diazonium chlorides. The former are much more photosensitive, and more strongly coloured; for these reasons, it is unlikely that these compounds have the same ultraviolet spectrum and therefore the same structure. In the analogous case of *p*-hydroxyphenyldiazonium chloride and *p*-quinone diazide, the compounds have different ultraviolet spectra and structures [109].

A recent study of the ultraviolet spectra of *p*-amino-substituted salts and of their conversion into *p*-iminoquinone diazides [99,111] showed that the latter absorb in a more longwave region of the spectrum than the corresponding *p*-amino-substituted diazonium salts (Table 7).

The ultraviolet spectra obtained by Anderson and coworkers are characteristic only of *p*-amino-substituted diazonium cations [160,161]. Anderson and coworkers did not succeed in obtaining the ultraviolet spectra of *p*-iminoquinone diazides, with the exception of the spectrum of one compound, because they did not sufficiently closely observe the conditions under which these compounds exist. When these conditions were observed (the diazo-solution was adjusted to pH 11.8 with NH_4OH), Anderson and Steedly found [160] that the spectrum of the diazonium salts *p*-$C_6H_5NHC_6H_4N_2HSO_4$ differed from that of the *p*-iminoquinone diazide *p*-$C_6H_5NC_6H_4N_2$, the latter absorbing in the more longwave region.

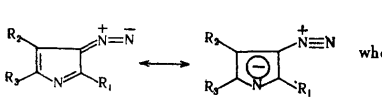
The values of ν_{CN_2} in the infrared spectra of *p*-iminoquinone diazides are close to the value for the cumulated C=N=N bond, and the values for *p*-amino-substituted diazonium salts are close to the value for the triple C−N≡N bond (see Table 7), but lower than the values for other aryldiazonium salts [99]. These results show that the structure of *p*-amino-substituted diazonium cations is close to the benzenoid form, but the structure of the *p*-iminoquinone diazides is close to the quinonoid form. But the ordinary formulae do not accurately reflect the structures of these compounds. Although the structure of *p*-iminoquinone diazides is closer to the quinonoid form in comparison with the initial *p*-amino-substituted diazo-compounds, this structure has a greater or lesser tendency to approach the benzenoid form, according to the electron-acceptor properties of the substituent:



This is reflected in an increase in the values of ν_{CN_2} in the infrared spectra and in a displacement of the ultraviolet absorption band towards the shortwave side (see Table 7).

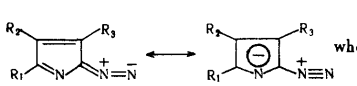
Little information has been published on the physicochemical properties and structure of *p*-iminoquinone diazides, and they have generally been much less studied than the more accessible quinone diazides. However, the study of these compounds is of undoubted practical and theoretical interest.

According to Tedder and Webster, the structure of heterocyclic diazo-imines is represented by a resonance hybrid [94,95].



where

R_1	R_2	R_3	ν_{CN_2}, cm^{-1}
Ph	NO_2	Ph	2150
Ph	H	Ph	2095
Ph	H	CH_3	2062

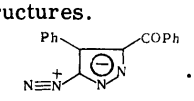


where

R_1	R_2	R_3	ν_{CN_2}, cm^{-1}
Ph	H	Ph	2138
Ph	NO_2	Ph	2172

Values of ν_{CN_2} have not been compared with those of the corresponding diazonium salts, although these salts have been separated in some instances [94].

Farnum and Yates [93] consider that the diazo-pyrazoles have structures close to the intra-ionic form, because the ν_{CN_2} values for these compounds are higher than those for the diazo-ketones, and close to those for the diazonium salts; however, they do not deny the possibility of resonance of two structures.



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BULK POLYMERISATION OF VINYL MONOMERS AT HIGH EXTENTS OF REACTION

G.P.Gladyshev and S.R.Rafikov

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I. INTRODUCTION

The study of bulk polymerisation at high extents of reaction is of both theoretical and practical interest. Although polymerisation to high conversions is often encountered in daily practice, relatively little systematic work has been done on this problem, in contrast to the initial stages of the polymerisation reaction, mainly because of the complexity of the quantitative interpretation of the results.

Nowadays there are semiquantitative theories which explain, on the whole satisfactorily, the characteristic features of polymerisation at advanced stages of the reaction. However, many problems still remain unsolved, which, for example, makes it impossible to control the "gel effect" in the polymerisation of important vinyl monomers such as methyl methacrylate, butyl methacrylate, etc.

The present review deals with the polymerisation of vinyl compounds not accompanied by the appearance of a new phase. Problems concerning the appearance of a new phase in ω-polymerisation, polymerisation of monomers whose polymers are insoluble, etc. are not included. The literature on these problems can be found in a number of monographs [1-3].

II. GENERAL THEORY OF THE "GEL EFFECT"

At the end of the 1930's it was observed that bulk polymerisation of certain vinyl monomers involves a sharp increase of reaction rate on attainment of certain degrees of conversion of the monomer into the polymer [1-18]. This phenomenon was called the "gel effect" or the "Trommsdorff effect". In the polymerisation of methyl methacrylate the acceleration usually occurs on attainment of about 15–25% conversion. In the polymerisation of substances whose polymers are insoluble in the monomers the reaction rate increases immediately after the formation of appreciable amounts of the polymer. The shape of the kinetic curves for polymerisation with self-acceleration is determined by the nature of the monomer, the concentration of the initiator, and the reaction conditions.

Initially it was believed that the increase in reaction rate is due to the process being non-isothermal [2,16]. It was suggested that the heat evolved during polymerisation raises the temperature of the reaction mass. However, this view soon had to be rejected [13,17]. Firstly, it was shown that polymerisation under strictly isothermal conditions also involves considerable self-acceleration. Secondly, it was established that in the acceleration stage the molecular weight of the polymers formed increases, whereas according to the equation

$$\frac{d\ln P}{dT} = \left(E_r - \frac{1}{2}E_0 - \frac{1}{2}E_{in}\right)/RT^2 \qquad (1)$$

the increase in polymerisation temperature in a chemically initiated reaction should in fact lower the molecular weight.

Norrish and Smith [17] suggested that the reason for the self-acceleration is the decrease of the rate constant k_t for the chain termination reaction. They showed that an increase of the initiator concentration or temperature in the polymerisation of methyl methacrylate displaces the onset of self-acceleration towards higher degrees of conversion. Since an increase of temperature and initiator concentration results in a lowering of the molecular weight of the polymer and hence of the viscosity of the medium, it is evident that the change in k_t is associated with an increase in viscosity.

To confirm these findings, Norrish and Smith [17] studied the polymerisation of methyl methacrylate in the presence of various solvents and established that systems of low viscosity exhibit the smallest self-acceleration. As suggested, the molecular weight of the polymers increased with the viscosity of the medium. Similar ideas about the possibility of a decrease of the rate constant for chain termination were put forward by Medvedev and coworkers [18], who studied the polymerisation of chloroprene.

Somewhat later Schulz and Harborth [19] made a detailed study of the polymerisation of methyl methacrylate in the presence of benzoyl peroxide and established that the rate of reaction in the later stages can exceed the initial rate of polymerisation by several tens. By varying the concentration of the peroxide, they showed that the maximum rate of polymerisation at the self-acceleration stage is directly proportional to the initial rate. Their explanation of the phenomenon of self-acceleration was the same as that of Norrish and Smith [17].

Trommsdorff and coworkers [15] established that introduction of poly(methyl methacrylate) into the monomer causes self-acceleration at the very beginning of the polymerisation reaction. Furthermore, they showed that if the system is cooled sharply to -20° at the self-acceleration stage and then reheated to the previous temperature a long time afterwards, the rate of reaction is the same as before the freezing. These data also confirm the general theory of the "gel effect".

On the other hand, the rate of polymerisation is determined by the rate of chain growth which can also vary with the viscosity of the medium. However, if allowance is made for the fact that the molecular size of the monomer is small compared with that of the macroradicals whose interaction leads to chain termination, it may be assumed that the variation of k_p during polymerisation is slight when the degree of reaction is low. An appreciable change of k_p at a degree of reaction of the order of 50–70% might be expected. Schulz and Harborth [19], who noted a sharp decrease in the rate of polymerisation at degrees of conversion exceeding 70–80%, arrived at this conclusion.

Thus a quantitative theory of the "gel effect" was developed at the end of the 1930's and the beginning of the 1940's of the present century. A quantitative test of the theory became possible only after the development of methods for the determination of the rate constants for the fundamental reaction steps.

III. QUANTITATIVE DATA

After the rotating sector and thermometric methods began to be used to determine the ratio k_p/k_t in chain polymerisation, papers dealing with the variation of k_p and k_t with the degree of conversion appeared. Matheson and coworkers [20-22] were the first to make reliable measurements (rotating sector method) and confirmed quantitatively the treatment of the "gel effect" proposed by Norrish, Smith, Schulz, and others. The study of the polymerisation of methyl methacrylate [22] showed that at 33% conversion the chain propagation rate constant remains virtually unchanged, whereas the chain termination constant decreases by a factor of more than a hundred. On the other hand, in the study of the photopolymerisation of

methyl acrylate in the presence of diacetyl and azobisisobutyronitrile, Matheson and coworkers[22] found that the rate of polymerisation increases continuously from the very beginning of the reaction. By comparing their results with the data of other investigators, they confirmed the theory of Norrish, Smith, and coworkers. Similar results were also obtained in the polymerisation of styrene, but the change in the ratio k_p/k_t was much smaller than for methyl methacrylate. This is due to the almost complete absence of the "gel effect" in the polymerisation of styrene. The percentage conversion at which self-acceleration begins is determined by the molecular weight of the polymer formed, and hence by the viscosity of the medium. The ratios $k_p(35\%)/k_p(0\%)$ and $k_t(35\%)/k_t(0\%)$ obtained by Matheson and coworkers[22] are given in Table 1.

Naylor and Billmeyer[23] obtained interesting data on the variation of the molecular weight of poly(methyl methacrylate) with the degree of reaction in photopolymerisation. They emphasised that the observed increase in the degree of polymerisation is associated with a decrease in the rate of termination of the polymeric chain and should be accompanied by a variation of the molecular weight distribution as the monomer is converted into polymers. Examination of the "percentage conversion–(time)(intensity)$^{1/2}$" relation clearly showed that, as the intensity of irradiation increases, the onset of self-acceleration becomes more distinct and is observed at increasing degrees of conversion. At high irradiation intensities the molecular weight of the polymer is lower than at low intensities. Hence it follows that for the same degree of conversion the viscosity of the medium is smaller in the former case and the acceleration should occur at higher degrees of conversion. These authors concluded that the use of light filters makes it possible to control the "gel effect". Somewhat later Pravednikov[24,25] confirmed the theory of Norrish, Smith, and others and noted that the interpretation of the self-acceleration phenomenon as a consequence of the formation of a three-dimensional polymeric network[26] is incorrect.

Melville[27] and Bengough[28] showed, using the thermocouple method, that in the polymerisation of vinyl acetate k_t decreases by a factor of three at 50% conversion, whereas k_p remains virtually unchanged (Table 2).

TABLE 1. "Gel effect" in the polymerisation of certain monomers.

Monomer	Temperature, °C	Conversion corresponding to onset of self-acceleration, %	$\frac{k_p(35\%)}{k_p(0\%)}$	$\frac{k_t(35\%)}{k_t(0\%)}$	Degree of polymerisation, P_{limit}
Vinyl acetate	25	>40	—	—	2400
Styrene	50	30	0.67	0.075	4000
Methyl methacrylate	30	15	1.12	0.0066	5000
Methyl acrylate	30	0	—	—	10000

TABLE 2. Photopolymerisation of vinyl acetate at 25° in the presence of the dinitrile of 1,1-azodicyclohexylcarbonic acid.

Conversion, %	k_p, litre mole^{-1} s^{-1}	$10^{-6}k_p$ litre mole^{-1} s^{-1}	E_p, kcal mole^{-1}	E_p kcal mole^{-1}
4	860	240	4.2	1
23	990	126	4.2	1
46	1070	90	3.6	3.9
57	238	6.7	8.6	11.8
65	30	1.15	11.4	13.0
73	—	—	14.4	15.4

TABLE 3. Polymerisation of butyl acrylate at 25° (rate of initiation 2.1 × × 10^{-8} mole litre^{-1} s^{-1}).

Conversion, %	$10^{-6}k_p$	$10^{-8}k_t$
1	2.93	4.8
20	0.76	0.38
40	0.46	0.115
60	0.26	0.43
70	0.0044	0.0073

There is an analogous variation of the activation energy for the chain propagation and termination reactions. Similar results were obtained for butyl acrylate and methyl methacrylate. In the polymerisation of butyl acrylate it was established that the reaction rate increases slightly with the degree of conversion, the fall in rate beginning at 20–30% conversion. Table 3 presents data on the variation of k_p and k_t and shows that the decrease of k_t is accompanied by a sharp decrease of k_p. In the authors' view this fact is associated with the structure of the polymer which is responsible for the "gel effect" at degrees of conversion much smaller than 20%. In the polymerisation of methyl methacrylate it was found[27] that k_t begins to decrease at about 20% conversion, whereas the decrease of k_p does not begin until the degree of conversion is about 50%.

Later Bengough and Melville[29] showed that, for the polymerisation of methyl methacrylate, the exponent n in the equation

$$V = kI^n[M] \qquad (2)$$

(I is the intensity of irradiation or the concentration of the sensitiser) decreases from 0.5 at 0–15% conversion to about 0.3 at 15–25% conversion, and then increases again and reaches 1 when the degree of conversion is of the order of 40%. It was also found that increase of conversion from 0 to 35% (at 32°) results in an increase of $10^5k_p/k_t$ from 1.9 to 110, whereas k_t decreases from 5.7×10^6 to 8.8×10^4 (litre mole^{-1} s^{-1}). Recently Hayden and Melville[30] confirmed these data. They found that at 10–40% conversion n decreases to 0.25, the activation energy for chain termination increases appreciably, while k_p and E_p remain constant. At a conversion in excess of 50% n increases, k_t and k_p decrease, and E_t and E_p increase.

Fujii[31,32] made a novel study of the polymerisation of styrene and methyl methacrylate at high extents of reaction and demonstrated that the lifetime of free radicals in viscous media can be conveniently calculated from the photochemical after-effect. He used the equation

$$\ln\left(\frac{V_p+V_\alpha}{V_p-V_\alpha}\right) = \ln\left(\frac{V_{pL}+V_\alpha}{V_{pL}-V_\alpha}\right) + 2\frac{V_\alpha}{V_{pL}}\frac{t}{\tau}, \qquad (3)$$

derived on the hypothesis that after irradiation ceases radicals are destroyed according to the law

$$-\frac{d[R\cdot]}{dt} = k_t[R\cdot]^2 - k_i[M]^2, \qquad (4)$$

where V_α is the steady-state rate of thermal polymerisation, V_p the rate of polymerisation at the instant t after irradiation is switched off, V_{pL} the steady-state rate of photopolymerisation, and the other symbols have the usual significance.

It follows from Eqn. (3) that the plot of

$$\frac{V_{pL}}{2V_\alpha}\ln\left(\frac{V_p+V_\alpha}{V_p-V_\alpha}\right)$$

against t makes it possible to determine $1/\tau$ and hence the lifetime of free radicals and the ratio k_p/k_t. The results are presented in Table 4.

Fujii also showed that the order of the chain-termination reaction decreases from 1.9–2.1 to 1.4–1.6 when the conversion increases from about 0 to 68%. These results are consistent with the data of Melville and coworkers[29,30]. Similar results were obtained in the polymerisation of methyl methacrylate[32] (Table 5). The order of the chain termination reaction for this monomer decreases from 1.9–2.1 to 1.65–1.8 when the conversion rises from 0 to 60%. In the polymerisation of styrene[31] and methyl methacrylate[32] the apparent activation energy decreases with percentage conversion.

Miyama[33-36] used a thermistor method to determine the variation of k_p/k_t with percentage conversion in the polymerisation of vinyl monomers. Fujii and Tanaka[37] obtained interesting results by measuring the lifetime of free radicals in the photopolymerisation of styrene in the presence of carbon tetrachloride. The addition of carbon tetrachloride tends to increase the initial rate of polymerisation but at high degrees of conversion it reduces the lifetime of macroradicals.

In order to reconcile the data on the variation of k_t and k_p with the degree of polymerisation and the molecular weights obtained, Robertson[38], who studied the kinetics of the polymerisation of styrene and methyl methacrylate, assumed that the effectiveness of initiation f varies with the degree of reaction. It was shown that, as polymerisation proceeds, f for many of the initiators investigated (benzoyl peroxide, azobisisobutyronitrile, t-butyl peroxide, and lauroyl peroxide) falls sharply and becomes very small when the percentage conversion is more than 50–60%.

TABLE 4. Photopolymerisation of styrene*.

Conversion, %	Temperature, °C	k_p/k_t	$k_{t(x\%)}/k_{t(0\%)}$
0	20	$0.55\cdot10^{-6}$	
38±1	30	$2.36\cdot10^{-6}$	1
43±2	30	$6.36\cdot10^{-4}$	$3.75\cdot10^{-3}$
	30	$2.56\cdot10^{-3}$	$9.22\cdot10^{-4}$
60±2	30	$1.30\cdot10^{-2}$	$1.81\cdot10^{-4}$
70±2	30	$1.37\cdot10^{-2}$	$1.71\cdot10^{-4}$

* Intensity of irradiation 4×10^{-8} einstein s^{-1}.

TABLE 5. Photopolymerisation of methyl methacrylate*

Conversion, %	Temp., °C	k_p/k_t	$k_{t(x\%)}/k_{t(0\%)}$
0≃1	30	$1.93\cdot10^{-5}$	1
	40	$2.47\cdot10^{-5}$	
47±2	30	$9.20\cdot10^{-3}$	$2.10\cdot10^{-3}$
52±2	30	$9.33\cdot10^{-3}$	$2.07\cdot10^{-3}$
	40	$9.48\cdot10^{-3}$	
	50	$9.86\cdot10^{-3}$	
72±3	30	$2.96\cdot10^{-2}$	$6.52\cdot10^{-4}$

* Intensity of irradiation 4×10^{-8} einstein s^{-1}.

Calculations of f in the polymerisation of styrene in the presence of azobisisobutyronitrile were also made by Nishimura[39], who used the equation

$$\bar{P}_n = \frac{[M]_0}{f[c]_0}\times\frac{x}{1-\exp(-k_d t)}, \qquad (5)$$

where $\bar{P}_n$ is the cumulative degree of polymerisation, $[c]$ the initiator concentration, k_d the initiator breakdown rate constant, and x the extent of reaction. A similar calculation was also made with allowance for the change in volume with the extent of reaction. However, Nishimura believes that the variation of f is only apparent.

After many data had accumulated on the effect of the extent of reaction of vinyl monomers on the kinetic constants of the fundamental reaction steps, it became necessary to relate quantitatively the changes in these parameters to the viscosity of the medium. The first serious attempts in this field were made by Vaughan[40] and Schulz[41,42]. Schulz examined Smoluchowski's equation and showed[41] that the rate of chain termination by reaction between radicals may be determined by diffusion even in media of relatively low viscosity. The rate of chain growth should be limited by diffusion only in media of very high viscosity. The results of Schulz's theoretical study were subsequently used by a number of investigators. Fujii[31] noted that the decrease of the overall activation energy with the extent of reaction is associated with the increase of the activation energy for chain termination:

$$E = E_p - \tfrac{1}{2}E_0 + \tfrac{1}{2}E_i.$$

Using the equation proposed by Spencer and Williams[43],

$$\eta = 3.63\times10^{-10}\exp\{0.0572\sqrt{M} + \sqrt{W_2}(22.54-0.045\sqrt{M}+5000/T)\} \qquad (6)$$

(where η is the viscosity of the styrene–polystyrene system in centipoises, M the molecular weight determined by the Staudinger method, and W_2 the weight fraction of the polymer), Fujii estimated the activation energy for the diffusion of polymeric polystyrene radicals for 38 and 60% conversion. He obtained 6.1 and 7.7 kcal $mole^{-1}$ respectively, which in his view is in good agreement with experiment and confirms the conclusion that the rate of the chain termination reaction is determined by diffusion. Fujii[32] also estimated the activation energy for chain termination in the polymerisation of methyl methacrylate (5.8 kcal × × $mole^{-1}$) for 52% conversion. This value is in good agreement with the data of Spencer and Williams[43] and the activation energy for viscous flow of fused polyesters, which according to Flory[44] is about 8 kcal $mole^{-1}$.

Miyama[36] made a detailed study of the effect of the viscosity of the medium on the kinetic constants for vinyl polymerisation. He expressed doubt about the correctness of the equation derived by Vaughan[40] on the basis of the theoretical study of Rabinowitch[45]. Miyama showed that the use of Smoluchowski's equation[46] for the number of collisions in solution makes it possible to obtain an expression relating the second-order rate constant to the viscosity of the medium. Comparison of the experimental values of k_p/k_t with η of the medium yields the following expressions:

$$(k_t)_{0\%}/k_t = 0.76 + 0.24\,[(\eta/\eta_0)^{0.30}\times10^{-8}(\eta/\eta_0)^{1.50}] \qquad (7)$$

(for vinyl acetate)

$$(k_t)_{0\%}/k_t = 0.83 + 0.17\,(\eta/\eta_0)^{28} \qquad (8)$$

(for methyl methacrylate)

The following formula is valid for the values of $(k_p)_{0\%}/k_p$ in the polymerisation of vinyl acetate[36]:

$$(k_p)_{0\%}/k_p = 1 + 0.65 \times 10^{-6}(\eta/\eta_0) \quad (9)$$

In Eqns. (7)–(9) the subscript 0% refers to zero percentage conversion. Miyama noted that the analysis of his data on the basis of the Rabinowitch equation gives unsatisfactory results. Starting in 1959, North and others published a series of papers in which they described a thorough investigation of the effect of the medium on the rate constants for vinyl polymerisation and in which they make a comprehensive examination of the mechanism of the chain termination process whose rate is determined by diffusion[47-52]. These studies led to important conclusions.

In order to eliminate the effects of branching and cross-linking, in their attempts to elucidate the effect of viscosity on polymerisation processes Benson and North[47] studied the relevant reactions in solvents of high viscosity. The ratio k_p/k_t was determined by the photochemical after-effect method. Later they calculated the ratio k_t/k_p^2 and hence k_t and k_p on the basis of a study of the dependence of the degree of polymerisation on the rate of reaction. The earlier postulate that the viscosity of the medium affects only k_t and not k_p (in media with a viscosity exceeding by a factor of several hundred the viscosity of the monomer) was confirmed. The study showed that in the range of η values from 0.400 to 1000 cP (methyl methacrylate) there is a linear relation between k_t and the viscosity of the medium. A relation of this kind was not observed for n-butyl acrylate. Thus the rate of chain termination in the polymerisation of methyl methacrylate is determined by diffusion even in a medium of low viscosity, comparable with the viscosity of the monomer, whereas in the polymerisation of n-butyl acrylate in media of relatively low viscosity k_t is independent of the viscosity and the reaction occurs in the "kinetic" region (k_t is then the rate constant of a chemical step). Only in media with viscosities in excess of about 10 cP is the rate of chain termination determined by diffusion.

The authors examined the results obtained within the framework of a three-step mechanism of radical reaction which they proposed[47]. It was shown that this mechanism leads to the equation

$$\frac{1}{k_t} = \frac{\eta}{k_{d'}} + \frac{1}{k_{c'}} \quad \text{or} \quad k_t = k_{c'} - \frac{k_{c'}}{k_{d'}}(k_t\eta), \quad (10)$$

where $k_{d'}$ and $k_{c'}$ are constants evaluated in the derivation of the relation between k_t and $k_t\eta$. Three possible models of bimolecular reactions are examined in the same study[47]. Later North and Reed[48] confirmed the earlier data showing that the rate of the chain termination reaction in the polymerisation of certain vinyl monomers is determined by diffusion even in media of low viscosity, comparable with the viscosity of the monomer[47,53,54]. In the polymerisation of methyl methacrylate the opposite relation between k_t and the viscosity of the medium was observed[48]. This effect is not due to the chemical nature of the solvent and the shape of its molecules. The results can be explained in terms of a two-stage diffusion-dependent chain termination process. Comparison of the diffusion-dependent chain termination rate constants and the diffusion coefficients of poly(methyl methacrylate) as a function of the concentration of the latter showed that the rate-determining stage of the process is segmental diffusion of the ends of the polymeric radicals and not translational diffusion (diffusion of the centres of gravity) of the macroradicals. It was also established that the chain termination process is influenced by the molecular weight and the concentration of the polymer in solution.

The studies of North and coworkers led to the paradoxical conclusion[48] that the rate of chain termination is determined by diffusion even when the conversion is only 0%, whereas self-acceleration becomes appreciable for conversions of the order of several per cent or even several tens per cent (styrene). However, North and Reed[48] showed that this apparent paradox is caused by inadequate allowance for the viscosity of the "segment–solvent" microregions.

Recently Benson and North[49] demonstrated that the rate constant for diffusion-dependent chain termination is a function of the chain length of the reacting radicals. They examined two models of segmental diffusion. The first leads to reasonable termination rate constants but is inconsistent with kinetic data. In the examination of the second model it was assumed that segmental diffusion depends on chain length until the latter exceeds a certain characteristic value N_L. After that segmental diffusion no longer depends on the chain length. If N_L is smaller than the average length of the kinetic chain, then

$$k_t = (4P_{AB}kT/3\eta)(R_E/x_0N_L^{1/2}), \quad (11)$$

where P_{AB} is a multiplier equal to 1/8, R_E is the effective distance between the ends of the chains in the transition state, and x_0 is a proportionality constant of the order of 2.2 Å. It follows from Eqn. (11) that the chain termination rate constant is a function of T/η, i.e.

$$k_t = f(T/\eta). \quad (12)$$

Calculations by Eqn. (11) are in satisfactory agreement with experiment. For example, for a monomer of the type of styrene η = 0.5 cP (R_E/x_0 = 1.4, N_L = 100). Hence at 300°K $k_t = 1.1 \times 10^8$ litre mole^{-1} s^{-1}. If the chain length is small and ν (the kinetic chain length) $< N_L$, the polymerisation kinetics cannot be described by the usual equations.

Later North and Reed[50] yet again confirmed their theoretical findings. They showed that in the polymerisation of methyl, n-butyl, isobutyl, and 3,5,5-trimethylhexyl methacrylate in solvents of different viscosity the rate of chain termination is determined for all alkyl methacrylates by the segmental diffusion of the ends of the macroradical chains. In media with viscosities between 0.42 and 5.72 cP k_t/k_p for the polymerisation of the above monomers is proportional to η^{-n}, where n = 1 for methyl methacrylate and $n < 1$ for the other alkyl methacrylates.

Allen and Patrick[55] examined the effect of diffusion on chain propagation and chain transfer reactions for high degrees of conversion. Using the previously published data[56] they showed that the usual hypothesis according to which the rate of chain propagation (transfer) at high extents of reaction is determined by diffusion is inconsistent with the diffusion coefficients of small molecules in polymers. Indeed it is known[56] that the diffusion coefficient D of small molecules (monomer) in a polymeric network is of the order of 10^{-7} cm^2 s^{-1}, whereas a much lower value is necessary for the rate of chain propagation ($k_p < 10^3$) to be determined by diffusion.

Guzman and Tratou[57] analysed the self-acceleration in the photopolymerisation of vinyl acetate in terms of the

Rabinowitch and Smoluchowski equations and derived the following relation on the basis of experimental data:

$$\frac{k_t}{k_t^*} = 0.97 + 0.03(\eta/\eta_0)^{0.41}, \quad (13)$$

where k_t is the chain termination rate constant without allowance for diffusion and k_t^* the value of k_t found experimentally. They state that the diffusion of macroradicals becomes rate-limiting in the process when the extent of reaction is of the order of 2%.

Guertin[58] obtained kinetic equations taking into account the effect of viscosity on the chain-termination reactions in free-radical polymerisation. He also showed that chain transfer results in a decrease of the "gel effect" because the former is independent of the viscosity of the medium, like the chain termination reaction.

Ryabov and others[59,60] showed that the rate of copolymerisation of methyl methacrylate with methacrylic acid begins to increase appreciably when the viscosity of the medium is 100–500 P which in their view is evidence of a considerable decrease of the rate of diffusion of macroradicals[60]. They believe that the onset of self-acceleration is determined solely by the viscosity of the medium and is independent of the nature and concentration of the initiator.

IV. CHAIN TRANSFER REACTIONS

The general theory of the "gel effect" does not take into account the effect of the chain transfer reactions on the polymerisation at high degrees of conversion. Relatively little work has been done on this problem[23,61,62]; among the papers dealing with this question, the excellent review of Pyrkov and Frenkel'[61] may be mentioned.

As the degree of conversion of the monomer into the polymer increases, the role of the chain transfer reactions via the polymer molecules increases too. Evidently this phenomenon is associated with the increase in the concentration of the polymer in the system. Furthermore, it may be that the rate constant for chain transfer via the polymer depends on the degree of polymerisation which increases with the degree of conversion. Schulz and others[3,63,64] showed that in the polymerisation of methyl methacrylate the rate constant for chain transfer via the polymer varies significantly with the molecular weight of the polymer, decreasing as the latter increases. This phenomenon is due to the fact that chain transfer occurs mainly via the terminal groups formed in chain termination by disproportionation and not via groups containing the initiator fragment. One of the proofs of the validity of this hypothesis is that the rate constant for chain transfer via the polymer is independent of the nature of the initiator (benzoyl peroxide, azobisisobutyronitrile). The rate constants for chain transfer via inner and terminal groups may be expressed by the equations

$$\left(\frac{k_{tr}}{k_p}\right)_{\text{inner}} = 2.2 \times 10^{-4},$$

$$\left(\frac{k_{tr}}{k_p}\right)_{\text{terminal}} = 0.10.$$

We may note that the results of Schulz and others do not exclude the possibility that the initiator affects the structure of the polymers synthesised. In their study of the polymerisation of styrene, Henrici-Olivé and Olivé[65-69] noted that the degree of polymerisation is higher at high extents of reaction than would be expected from the reaction rate. This phenomenon may be explained if it is assumed that the relative contribution of the chain transfer reaction in the reaction between primary radicals and macromolecules increases with the degree of conversion:

$$R_{per}^{\cdot} + P \rightarrow RH + P^{\cdot}$$
$$P^{\cdot} + n\mathrm{M} \rightarrow \text{branched polymer.}$$

Thus in the polymerisation of styrene in the presence of azobisisobutyronitrile at 50° the average number of initiator fragments per polymer molecule increases from 2.03 to 2.48 when the degree of conversion rises from 0.05 to 0.93. The chain transfer reactions can result in an apparent change of the effectiveness of initiation (calculated from the molecular weight of the polymer) with the degree of conversion. Chain transfer via the polymer results in an anomalous increase of the molecular weight of the latter and the value of f calculated from Eqn. (5) may be too low.

V. NEW THEORETICAL POSTULATES

Examination of the quantitative data obtained by Norrish, Smith, and Schulz shows that the problem of setting up a rigorously quantitative theory of the "gel effect" is extremely complex. Nevertheless, a number of investigators attempted to develop other semiquantitative theories[70-74]. The first serious attempt was made by Burnett and coworkers. They suggested[70] that the phenomenon of self-acceleration may be explained from the standpoint of a change in the concentration of the growing radicals in the polymerisation. Burnett and coworkers[70,71] demonstrated that the rate of polymerisation of methyl methacrylate is a linear function of percentage conversion when the latter is in the range 20–60%. The overall activation energy for the process falls initially as polymerisation proceeds and then increases sharply:

Conversion, %	0	19	30	36	41	50	57	62	67	71
E, kcal mole^{-1} (25–60°)	5.2	4.7	3.4	2.7	2.0	1.7	3.1	4.1	5.0	8.4

The exponent n in the rate equation for the reaction is initially 0.5 and then falls, it passes through a minimum at about 20% conversion, and increases again to 0.8 at about 60% conversion. These results are consistent with the data of Bengough and Melville[29] and show that chain termination is not a second-order reaction. Hence it follows that the old interpretation of the results of studies on bulk polymerisation lacks reliable justification, since the kinetic expressions used presuppose that chains are destroyed as a result of their interaction. The explanation of the "gel effect" must be sought in the change of the concentration of macroradicals during polymerisation and not only in the possible change of the rate constants for the fundamental reaction steps. Polymerisation results in an increase of the viscosity of the medium and macroradicals can no longer react with one another. At not too high extents of reaction the monomer molecules diffuse towards macroradicals and react with them. Thus the overall rate of reaction increases because of the lowering of the rate of chain termination and the increase of the rate of chain propagation. As already pointed out, the latter is more likely to be due to a change in the radical concentration than to a change in the rate constants for the fundamental reaction steps. Burnett and coworkers assumed that, starting with a certain degree of conversion, the rate of increase of the number of radicals is proportional to the

concentration of the polymer formed. Hence it follows that

$$d[R\cdot]/dx = k_1(x - x_1), \quad (14)$$

where $[R^{\cdot}]$ is the radical concentration, k_1 a constant, x the specific degree of conversion of the monomer into the polymer, and x_1 the critical degree of conversion, which depends on the molecular weight of the polymer formed in the initial stages.

Integration of Eqn. (14) gives

$$[R\cdot] - [R\cdot]_0 = \tfrac{1}{2}k_1(x - x_1)^2, \quad (15)$$

where $[R^{\cdot}]_0$ is the value of $[R^{\cdot}]$ where $x = x_1$. Eqn. (15) can be rewritten in the form

$$\frac{[R\cdot]}{[R\cdot]_0} = 1 + K_1(x - x_1)^2, \quad (16)$$

where $K_1 = \frac{1}{2}k_1(k_t/V_i)^{1/2}$ is a constant and V_i is the rate of initiation ($V_i = k_t[R^{\cdot}]^2$). Assuming that the concentration of the monomer near the growing radicals is constant, the following expression can be obtained instead of Eqn. (16):

$$(V_x/V_0 - 1)^{1/2} = K_1^{1/2}(x - x_1), \quad (17)$$

where V_x is the rate of polymerisation for a degree of conversion x and V_0 the initial rate of polymerisation.

It follows from Eqn. (17) that in the self-acceleration stage there should be a linear relation between $[(V_x/V_0) - 1]^{1/2}$ and x; the intercept made by the straight line on the abscissa should be equal to x_1 and its slope should be $K_1^{1/2}$. Eqn. (17) holds satisfactorily over a limited range of percentage conversions. At higher percentage conversions (about 50–60%) macroradicals become inaccessible to monomer molecules and the following equation then holds:

$$\frac{[R\cdot]}{[R\cdot]_0} = 1 + K_1(x - x_1)^2 - K_2(x - x_2)^2, \quad (18)$$

where x_2 is the second critical degree of conversion. Eqn. (18) can be written thus

$$[1 + K_1(x - x_1)^2 - V_x/V_0]^2 = K_2^{1/2}(x - x_2). \quad (19)$$

Hence it follows that there should be a linear relation between $[1 + K_1(x - x_1)^2 - V_x/V_0]^2$ and x. Burnett and Duncan[71] showed that this relation holds in the polymerisation of methyl methacrylate.

Similar results were obtained in the photopolymerisation of n-propyl and n-butyl methacrylates[72]. However, the polymerisation of methyl methacrylate[73] can be described by the above method only when allowance is made for additional factors characterising the possibility of the formation of branched and cross-linked structures.

The validity of the general postulates of Burnett and coworkers is evident. Clearly at high degrees of conversion a considerable increase in the lifetime of the polymeric radicals and hence an increase in their concentration may be expected. The electron spin resonance method made it possible to determine directly the concentration of radicals in viscous media. Many measurements of this kind were made[75–78]. For example, Bresler and coworkers[79], who made an ESR study of the photopolymerisation of methyl methacrylate, established that at high degrees of conversion the concentration of radicals exceeds 10^{-3} M. It should be noted that not all the radicals detected in the polymer–monomer system by the ESR method are equally stable. After irradiation ceases most of them vanish over a period of several minutes. The remaining radicals are stable and persist in the specimen at room temperature over a fairly long period.

Sawada[74] attempted to interpret quantitatively the results obtained in the study of the block polymerisation of methyl methacrylate. He started with the hypothesis that, if the radicals in a highly viscous medium become immobile and cannot disappear as a result of interaction with one another, their concentration should increase continuously as polymerisation proceeds. At a certain critical degree of conversion, the macroradicals are so firmly "stuck" in the polymer that they cannot react with the monomer.

If it is assumed that the concentration of radicals is proportional to the amount of monomer consumed since the onset of self-acceleration, the following expression holds:

$$[R\cdot] = K(x - b), \quad (20)$$

where K is a constant, x the degree of conversion of the monomer, and b the degree of conversion at which self-acceleration begins. On expressing the concentration of the monomer in terms of the critical degree of conversion a, i.e. putting

$$[M] = (a - x), \ (x < a) \quad (21)$$

and substituting the values of $[R^{\cdot}]$ and [M] from Eqns. (20) and (21) in the rate equation for the reaction, we obtain the equation

$$dx/dt = k_pK(x - b)(a - x). \quad (22)$$

Integration of Eqn. (22) yields

$$[1/(a - b)]\ln[(x - b)/(a - x)] = k_pKt + C, \quad (23)$$

where C is a constant. It follows from Eqn. (23) that $[2.3/(a - b)]\log[(x - b)/(a - x)]$ should vary linearly with time, which according to Sawada's data is borne out by experiment.

Allen and Patrick[75] examined the role of the so called "geminate chain recombination" in the kinetics of the polymerisation at high conversions.

Thus the explanation of the "gel effect" given by Norrish, Schulz, and other investigators presupposes the existence of a steady state throughout the bulk polymerisation process. However, the variation of the exponent n of the irradiation intensity in Eqn. (2) during polymerisation contradicts this hypothesis. It follows from the theory of Schulz and others that a higher value of k_t for a monomer should involve a more pronounced "gel effect". However, this is not in fact observed. Thus for styrene $(k_t)_{30\%} = 5.0 \times 10^7$ and for methyl methacrylate the corresponding value is 2.4×10^7. Nevertheless the "gel effect" in the polymerisation of methyl methacrylate is much more pronounced than in the polymerisation of styrene. The theory of Burnett and Duncan is more satisfactory. However, it is only qualitative and is based on purely empirical postulates. Although at the present time it is probably impossible to set up a rigorously quantitative theory because of the large number of factors involved in block polymerisation, a number of additional postulates must nevertheless be taken into account. Thus the majority of investigators do not consider the effect of the nature of the initiator on the polymerisation kinetics at high conversions. Also, frequently allowance is not made for the change in volume during polymerisation[80], the possible change in the rate of initiation associated with the increasing viscosity of the medium, and other factors.

At first sight it may appear that both in the initial stages and at high conversions the nature of the initiator is fairly

completely characterised by the rate constant k_d for the breakdown of the given initiator and the effectiveness of initiation f. In fact these quantities are never adequate for the description of the polymerisation process at high conversions[81]. It is well known that the following expression holds for catalysed polymerisation[1-8]:

$$-\frac{d[M]}{dt} = \frac{k_p}{k_0^{1/2}}(2k_d f)^{1/2}[c]^{1/2}[M], \quad (24)$$

where $[c]$ is the concentration of the initiator.

If the breakdown of the initiator is a first-order reaction, then obviously

$$-\frac{d[c]}{dt} = k_d[c]. \quad (25)$$

Furthermore,

$$[c] = [c]_0 e^{-k_d t}, \quad (26)$$

where $[c]_0$ is the initial concentration of the initiator. On substituting Eqn. (26) in Eqn. (24), we have

$$-\frac{d[M]}{dt} = \frac{k_p}{k_0^{1/2}}(2k_d f)^{1/2}[c]_0^{1/2}e^{-k_d t/2}[M]. \quad (27)$$

There is no doubt about the applicability of Eqn. (27) to polymerisation in many systems, both in the solid state and in solution, at low conversions[82,83]. However, Eqn. (27) no longer holds for polymerisation in viscous media. As polymerisation proceeds, the rate of initiation and the value of f in Eqn. (27) begin to vary. For example, Breitenbach and Frittum[84] showed that the rate of decomposition of the peroxide $(p\text{-}ClC_6H_4CO)_2O_2$ in polystyrene is lower than in solvents. Similar data were obtained by Haas[85-87]. Abdul-Said[2] showed that, when the viscosity of the solution is increased by a factor or ten, the rate of initiation falls by a factor of two. Dolgoplosk and coworkers[88] observed an increase in the yield of the recombination products of primary radicals in the decomposition of asymmetric diazo-compounds in viscous media. If the "gel effect" theory of Schulz and others is adopted, i.e. if allowance is made for the variation of the rate constants for the fundamental reaction steps with increasing viscosity and appropriate corrections to f are made, Eqn. (27) still need not always hold. The reason is that all the theories described above fail to take into account a number of factors. Thus allowance is not made for the possibility of chain termination when chains interact with primary radicals and for the chain transfer reaction. The possibility of chain termination by primary radicals during polymerisation has been pointed out in a number of papers[61,81,89-95]. The kinetic equations obtained with allowance for these processes differ considerably from the equations which follow from the usual theory[94,95]. Chain transfer reactions with participation of primary radicals at high conversions were studied by Henrici-Olivé and Olivé[65-69,101] and also other workers[58].

Theoretical examination shows that an increase in the viscosity of the medium lowers the rate of reactions in which large species participate (chain termination in the reaction of macroradicals) and has almost no effect (at least at 50–70% conversion) on the rate of processes involving small species (chain propagation, chain termination by primary radicals, chain transfer via initiator and low-molecular-weight inhibitor molecules, chain transfer with participation of primary radicals, etc.). Hence it follows that, as polymerisation proceeds, the relative role of processes involving the participation of small molecules should increase, which may lead to a decrease of the "gel effect"[81]. The reactivity of primary radicals will of course determine the nature of the "gel effect" on a par with other factors. However, for reasons stated above, account must also be taken of purely geometrical factors, namely the size of primary radicals which affects the diffusion coefficients.

In relatively non-viscous media the size of primary radicals has little effect on the capacity to participate in chain termination (transfer) reactions. This also applies to the value of f, which is associated with the possibility of recombination of primary radicals (cage effect). At high conversions the size of primary radicals determines both the possibility of their participation in the chain termination (transfer) reaction and the value of f. The relation between the effect of primary radical recombination and the viscosity of the medium is well known. For example, in his study of the decomposition of benzoyl peroxide in polymeric media, Haas[85-87] confirmed the postulates of the theory of primary recombination. On the other hand, it is evident that radicals such as $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, ..., C_nH_{2n+1} may participate in chain termination and transfer reactions to different extents because the diffusion coefficients may vary markedly with the size of the species[96].

It follows from the above considerations that the nature of self-acceleration at high conversions should be determined not only by the monomer but also by the initiator. Furthermore, the magnitude of the "gel effect" is determined by the concentration of the initiator and the experimental conditions. The "gel effect" may vary from one initiator to another[81]. Thus it has been established that bulk polymerisation of methyl methacrylate in the presence of peroxydicarbonates involves a smaller "gel effect"[97,98] compared with polymerisation in the presence of benzoyl peroxide, azobisisobutyronitrile, and other initiators. Similar results were obtained in a study of the polymerisation of methyl methacrylate activated by partial oxidation during exposure to ionising radiation[99], ultraviolet light[100], and visible light in the presence of sensitisers[101,102]. As already mentioned, such differences may be associated not only with different values of k_d and f for the given initiators but also with the different nature of the initiators themselves and the primary radicals which may participate in the chain termination and transfer reactions. The decrease of the "gel effect" at high conversions of the photo-activated monomer[100] is due to an increase of the effect of inhibitors and peroxide decomposition products formed during oxidation of the monomer. The differences in the nature of the "gel effect" during polymerisation in the presence of benzoyl peroxide, azobisisobutyronitrile, percarbonates, and hydrogen peroxide is due to the chain transfer and chain termination effects with participation of primary radicals. These conclusions were arrived at[81] by comparing the kinetic curves for polymerisation in the presence of the initiators enumerated above. Fig. 1 shows curves characterising the self-acceleration of the polymerisation of methyl methacrylate in the presence of the various initiators.

The data presented were obtained for equal concentrations of the initiators compared and therefore the differences are due to different values of k_d for the initiators and processes which are not usually taken into account by the theory. In order to eliminate the effect of k_d on the "gel effect", it is desirable to make the comparison for the same rate of initiation. Such data are presented in Fig. 2, which shows that the nature of the initiator has a significant effect on the magnitude of the "gel effect".

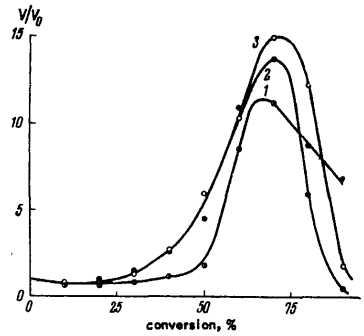

Fig. 1. Self-acceleration in the polymerisation of methyl methacrylate in the presence of various initiators at 60° and a constant initiator concentration (0.45 mole %):
1) dicyclohexyl peroxydicarbonate; 2) azobisisobutyronitrile; 3) benzoyl peroxide.

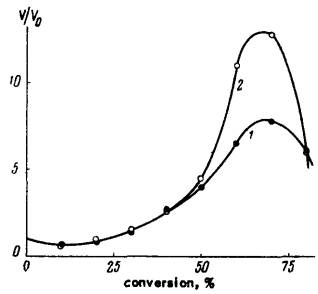

Fig. 2. Self-acceleration in the polymerisation of methyl methacrylate at 60° and constant initial rates of initiation:
1) dicyclohexyl peroxydicarbonate (0.045 mole %); 2) azobisisobutyronitrile (0.45 mole %).

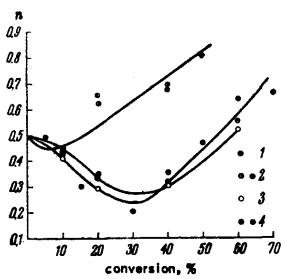

Fig. 3. Variation with the extent of conversion at 60° of the exponent n of the initiator concentration in the kinetic rate equation for the reaction, initiator — benzoyl peroxide:
1) n calculated for the initiator concentration range 0.0045–0.00045 mole %; 2) different series of experiments; 3) 0.045–0.0045 mole %; 4) 0.45–0.045 mole %.

It is difficult to allow for this effect quantitatively, but information about the chain transfer reaction may be obtained from a study of the molecular weight and polymer structure at different conversions. The possibility of chain termination by primary radicals can be assessed indirectly from the value of the exponent n of the initiator concentration (or irradiation intensity) in Eqn. (2)†. The variation of n with percentage conversion is determined by the nature of the initiator and its concentration (Fig. 3). These findings are in good agreement with the theory.

VI. OTHER STUDIES

There have been a number of investigations whose results confirm qualitatively the general theory of the "gel effect". Arbuzova and others [103] studied the photopolymerisation of acrylamide, methacrylamide, and hydroxymethylmethacrylamide in aqueous and glycerol solutions ($\lambda \simeq 3000$ Å). It was found that acrylamide and methacrylamide are polymerised only in glycerol. The rate of polymerisation of hydroxymethylmethacrylamide in glycerol is much higher than in aqueous solution. The authors explained these results on the hypothesis that the viscosity of the medium affects the rate constants for the termination of the polymeric chains. Later a similar phenomenon was observed in the polymerisation of acrylonitrile and other monomers but here initiation was effected at the interface between two phases [104]. Guzman and Delgado [105] studied the kinetics of the polymerisation of vinyl acetate at high conversions. The data obtained are consistent with the usual theory.

A number of investigators observed self-acceleration in the polymerisation of styrene [106–109]. A sharp increase in the molecular weight of the polymer was noted between 20 and 25% conversion [107,108]. The acceleration of the reaction in the case of methyl methacrylate and other acrylic esters was described by a number of investigators [106,110–115]. Burnett and coworkers [110] and also Matyska et al. [111] studied the polymerisation of n-butyl methacrylate. They established that self-acceleration occurs only after the attainment of about 40% conversion. A similar phenomenon was observed also for n-propyl methacrylate [112]. In their study of the copolymerisation of methyl methacrylate with methacrylic acid, Tarakanov et al. [113] showed that, as the methacrylic acid content of the system increases, the rate of polymerisation also rises; there is a corresponding increase in the maximum rate.

The general theory of the "gel effect" was also used in the treatment of the mechanism of three-dimensional polymerisation. Melville [27] and Melville and Hayden [30] were the first to study the effect of a three-dimensional polymer on self-acceleration at high conversions. It was shown that in the copolymerisation of methyl methacrylate with ethylene glycol dimethacrylate increase of the concentration of the latter results in onset of self-acceleration at lower conversions, while the rate of the chain termination reaction is determined by diffusion at zero conversion. Later Korolev and Berlin and coworkers made a detailed study of the three-dimensional polymerisation of a number of oligomers [116–122]; their results fully confirmed the validity of the general theory of polymerisation at high conversions. In addition, new data were obtained on the

† It should be noted that the variation of n with percentage conversion is also associated with the variation of the diffusion coefficient of macroradicals as the conversion changes [48].

characteristic features of three-dimensional polymerisation.

Thus it may be regarded as demonstrated[71,98] that the characteristic features of polymerisation at high conversions are not associated only with changes in the chain termination rate constant but with other kinetic parameters, namely the chain propagation rate constant, the rate of initiation, and the concentration of macroradicals. Furthermore, it was established that chain termination in the polymerisation of monomers such as methyl methacrylate, styrene, and others is diffusion-dependent even in the initial stages of the reaction[47,50].

At the same time the studies made in recent years show that the hypotheses described above are inadequate for the construction of a rigorously quantitative theory. For example, the available data are clearly inadequate for the interpretation of the absence of self-acceleration in the initial stages of the polymerisation of methyl methacrylate and other monomers[48]. The "paradox" considered above[48] may be explained if account is taken of the fact that in media of low viscosity not only the chain termination rate constant but also the effectiveness of initiation and the initiator breakdown rate constants vary[98,123]. The last two factors are also responsible for differences in the nature of acceleration during polymerisation in the presence of various initiators[98].

There are interesting possibilities in the study of many fundamental processes at high conversions. Thus it has been shown[124] that the study of inhibition processes in media of high viscosity permits a direct quantitative estimate of the reactivity of compounds which are relatively unreactive in radicals reactions. This cannot be done by other available methods. It is possible that further study of polymerisation at high conversions will lead not only to improved control methods for processes in which high conversions are attained[125] but also to some revision of the available data on polymerisation at low conversions[126].

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IVAN LYUDVIGOVICH KNUNYANTS

Dear Ivan Lyudvigovich,

Your collaborators, numerous pupils, and the Editorial Board of the Journal "Uspekhi Khimii" wish to convey to you their heartfelt greetings on the occasion of your 60th birthday. Your encyclopaedic knowledge, inexhaustible energy, brilliant talent for research work, and constant endeavour to investigate the unknown have made you one of the greatest organic chemists, whose work in a great variety of fields of organic chemistry has received world recognition. You have pioneered the youngest and most vigorously developing scientific field, the chemistry of organic compounds of fluorine, and have become the head of the Soviet school of organic fluoro-chemistry. Your work on the study of the synthesis of physiologically active substances and the study of the relation between their structure and biological action is also widely known.

Throughout your activities you have always conducted an active struggle in defence of scientific truth which earned you deep respect and recognition by the scientific community.

We wish you, dear Ivan Lyudvigovich, good health and new creative successes.

U.D.C. 547.321

ELECTROPHILIC ADDITION REACTIONS OF FLUORO-OLEFINS

B.L.Dyatkin, E.P.Mochalina, and I.L.Knunyants

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INTRODUCTION

The specific properties of fluoro-olefins, revealed in the unusual ease of their reaction with nucleophilic reagents (alcohols, amines, mercaptans, organomagnesium compounds, and others), are now well known and are no longer surprising; they find a natural explanation in the electron--acceptor effect of the fluorine atoms and the perfluoroalkyl groups, which is due both to the inductive effect and the conjugation effect. On the other hand, the electrophilic addition reactions, which are typical also for unsubstituted olefins, are hindered in the case of fluoro-olefins and for this reason they have been little investigated for a long time. However, in the course of development of organic fluoro-chemistry interest in reactions of fluoro-olefins with electrophilic reagents increased continuously. They attracted the attention of chemists both in connection with the theoretical study of the nature of the π bond of fluoro--olefins and for practical reasons, in connection with possible ways of synthesising new classes of organic fluoro-compounds. Numerous investigations carried out in recent years showed that the π bond in fluoro-olefins retains to a certain extent the nucleophilic properties characteristic of double-bonded carbon atoms, and fluoro--olefins are capable of reacting with various electrophilic reagents. As a rule, these reactions take place under comparatively severe conditions and require the application of effective catalysts; only when the electrophilicity of the reagent is very high can they occur under mild conditions and in the absence of catalysts.

However, it should be borne in mind that fluoro-olefins enter fairly readily into homolytic reactions and their interaction with certain electrophilic reagents, which can easily undergo fission into radicals, takes place predominantly by a radical mechanism. On the other hand, fluoro--olefins with pronounced electron-acceptor properties sometimes react by a nucleophilic addition mechanism even with substances which usually behave as electrophilic reagents. There is a fairly large number of examples of such "reversal of mechanism" and they are of special interest.

I. ADDITION OF HALOGENS

The addition of halogens to the double bond of fluoro--olefins occurs in most cases by a radical mechanism — as a result of a photochemical or thermal process. There are few examples of reactions whose conditions indicate an ionic mechanism (low temperature, the use of appropriate catalysts, etc.) and these involve mainly hydrogen-containing fluoro-olefins which have not yet lost their similarity to unsubstituted olefins.

Thus 1-chloro-1,2-difluoroethylene combines with bromine at -25°.[1] The addition of chlorine to trifluoroethylene at 100° in the presence of ferric chloride has been described[2]. Apparently the reaction did not really require such severe conditions, since it has been shown that bromine adds readily to trifluoroethylene at 20° in the dark without catalyst[3]. Vinylidene fluoride and tetrafluoroethylene are readily brominated at -10°.[4] 2-Trifluoromethylpropene and 1-chlorotrifluoromethylpropene combine quantitatively with chlorine in the dark in the presence of traces of ferric chloride[5].

The addition of halogens to perfluorovinyl ethers[6,7] and perfluorovinyl amines[6,8], where the electron density at the double bond is extremely high due to conjugation with the unshared electron pair of oxygen or nitrogen, is undoubtedly an electrophilic reaction:

$$CF_3-\overset{\curvearrowleft}{CF}=CF-\overset{\curvearrowleft}{O}-CH_3+Br_2 \xrightarrow{0^\circ} CF_3CFBrCFBrOCH_3,$$

$$CF_3-\overset{\curvearrowleft}{CF}=CF-\overset{\curvearrowleft}{N}(C_2H_5)_2+Br_2 \xrightarrow{0^\circ} CF_3CFBrCFBrN(C_2H_5)_2.$$

An ionic mechanism can be definitely invoked for the addition of mixed halogens, IF, BrF, ICl, and IBr, to fluoro-olefins†. These compounds are polar due to the different electron affinities of the halogens, which favours their heterolytic breakdown:

$$\overset{\delta+}{I} \rightarrow \overset{\delta-}{Cl} \rightarrow I^+ + Cl^-.$$

Indeed the greater the differen e in the electronegativities of the halogens the easier is the addition of the mixed halogens to fluoro-olefins. The addition of IF to the fluoro-olefins $CF_3CH=CF_2$,[9] $CF_2=CHF$,[10] $CF_2=CH_2$, perfluorocyclobutene[11], perfluorocyclohexene[11], and CFCl=CHF [1] proceeds in accordance with the polarisation of the reagents and in each case a single addition product is obtained in high yield. The ease of addition of iodine monochloride to fluoro-olefins decreases in the series[11]:

$$CF_2=CH_2 \; CF_2=CFCl \; \begin{array}{l} CF_2-CF \\ \| \quad | \\ CF_2-CF \end{array} \; \begin{array}{ccc} & CF_2 & \\ CF_2 & & CF \\ \| & & | \\ CF_2 & & CF \\ & CF_2 & \end{array} \; CF_3CF=CFCF_3.$$

The addition of IBr to $CF_2=CH_2$ [12] is also consistent with the polarity, a single product, CF_2BrCH_2I being obtained, while according to modern concepts concerning the stability of intermediate radicals the homolytic reaction should have given CF_2ICH_2Br. The addition of IF [13-15] and BrF [13] to fluoro-olefins occurs similarly, for example:

$$CF_3-CF=CF_2+IF \rightarrow CF_3CFICF_3.$$

More complex reactions take place in the addition of mixed halogens to chlorotrifluoroethylene $CF_2=CFCl$. The double bond of chlorotrifluoroethylene is polarised in such a way that a partial positive charge is concentrated at the difluoromethylene group, since, in consequence of the smaller length of the C–F bond compared with the C–Cl bond, the free electron pair of fluorine is involved in conjugation with the π electrons of the double bond to a greater extent than the free electron pair of chlorine.

According to the initial communications[16,17], the addition of iodine chloride to chlorotrifluoroethylene yields a single product, 1,2-dichlorotrifluoroiodoethane $CF_2ClCFClI$, whose formation is consistent with the polarity of the

† The stoichiometric mixtures $BrF_3 + Br_2$ and $IF_5 + I_2$ are used as the monofluorides of bromine and iodine.

reagents. However, a number of investigators subsequently showed[13,18-20] that as a rule both possible isomers are formed in proportions which depend on the temperature, the material of the reaction vessel, etc.

$$CF_2=CFCl+ICl \rightarrow CF_2ClCFClI+CF_2ICFCl_2.$$

These two modes of reaction were interpreted by one of the authors[18] as proof of a radical mechanism in the addition of ICl to $CF_2=CFCl$. Indeed, the addition of ICl to $CF_2=CFCl$ under the conditions of the homolytic reaction, in the gas phase under ultraviolet irradiation, gives a mixture of both isomers[21]. Nevertheless the two modes of reaction in liquid-phase processes are probably due to purely steric factors which permit electrophilic addition in a manner opposed to that dictated by the polarisation of the double bond[13]. Below it will be shown that the same reasons are responsible for two pathways in the condensation of chlorotrifluoroethylene with formaldehyde which is undoubtedly ionic.

The change in the mode of reaction when the mechanism is altered is clearly seen in the reaction of iodine chloride with trifluoroethylene, where in contrast to chlorotrifluoroethylene, the addition by ionic and radical mechanisms should lead to different isomers:

$$CF_2=CHF \xrightarrow{I^+} {}^+CF_2CHFI \xrightarrow{Cl^-} ClCF_2CHFI, \quad (I)$$

$$CF_2=CHF \xrightarrow{Cl\cdot} \cdot CF_2CHFCl \xrightarrow{I\cdot} ICF_2CHFCl. \quad (II)$$

In fact in the liquid-phase reaction compound (I) is formed almost exclusively whereas under ultraviolet irradiation the amount of compound (II) increases to 26–36%.[22]

A mixture of both possible isomers is formed when IF and BrF react with chlorotrifluoroethylene[13,14] and IF with the asymmetric dichlorodifluoroethylene $CF_2=CCl_2$.[23] The reasons for this phenomenon are probably the same as for the two modes of reaction of ICl with $CF_2=CFCl$.

Fluoro-olefins can enter into coupled addition reactions with halogens. Hydrogen-containing fluoro-olefins such as $CF_3CH=CH_2$, $CF_2=CHF$, and $CF_2=CH_2$ react with bromine in acetic acid in the presence of mercuric acetate or sulphate with formation of the acetates of the corresponding bromohydrins or their reaction products[24]:

$$CF_3CH=CH_2+Br_2+CH_3COOH \xrightarrow{Hg(OAc)_2} CF_3CHBrCH_2OCOCH_3,$$

$$CF_2=CFH+Br_2+CH_3COOH \xrightarrow{Hg(OAc)_2} CFHBrCF_2OCOCH_3,$$

$$CF_2=CH_2+Br_2+CH_3COOH \xrightarrow{Hg(OAc)_2} CH_2BrCF_2OCOCH_3.$$

The reaction in the presence of CCl_3COOH, CF_3COOH, and CHF_2COOH proceeds similarly[25]. The mechanism of the addition is undoubtedly the same as the mechanism of the familiar halogenation reactions of olefins in water, alcohol, or acetic acid, where the principal products are the halogenohydrins or their esters[26]:

The coupled addition of chlorine and fluorine to vinylidene fluoride occurs under the action of hexachloromelamine in anhydrous hydrogen fluoride[27]:

$$[-N=C(-NCl_2)-]_3+3HF \rightleftarrows [-N=C(-NH_2)-]_3+3Cl^++3F^-,$$

$$CF_2=CH_2 \xrightarrow{Cl^+} {}^+CF_2CH_2Cl \xrightarrow{F^-} CF_2CH_2Cl.$$

Recently it has also been shown that coupled addition of halogens to fluoro-olefins by a nucleophilic mechanism occurs under the action of potassium fluoride and iodine in an autoclave[28]:

$$>C=C< \xrightarrow{F^-} >C(F)-C^-< \xrightarrow{I_2} >C(F)-C(I)<.$$

Fluoro-olefins such as tetrafluoroethylene, hexafluoropropene, higher α-perfluoro-olefins, and perfluorocyclobutene enter into this reaction:

$$CF_2=CF_2 \rightarrow CF_3CF_2I,$$

$$CF_2=CF-CF_3 \rightarrow CF_3CFICF_3,$$

$$\begin{matrix} CF_2-CF \\ \| \\ CF_2-CF \end{matrix} \rightarrow \begin{matrix} CF_2-CF-I \\ | \quad | \\ CF_2-CF_2 \end{matrix}.$$

Perfluoroisobutene gives an 86% yield of perfluoro-t-butyl iodide under the action of potassium fluoride and iodine in nitrobenzene at 170°:[29]

$$(CF_3)_2C=CF_2 \rightarrow (CF_3)_3C-I.$$

Thus this method can be used for the coupled halogenation of fluoro-olefins which do not react with halogens under the conditions of the electrophilic reaction or react with difficulty.

II. ADDITION OF HYDROGEN HALIDES

There is a fairly large number of examples of the addition of hydrogen halides to fluoro-olefins by an electrophilic mechanism. In the first place this applies to hydrogen-containing fluoro-olefins. Thus 1,1-difluorobut-1-ene[30] and 1,1,3,3,3-pentafluoropropene[31] combine with hydrogen fluoride on heating without catalysts, in conformity with the polarisation of the reagents:

$$CH_3CH_2CH=CF_2+HF \xrightarrow{40^\circ} CH_3CH_2CH_2CF_3,$$

$$CF_3CH=CF_2+HF \xrightarrow{100^\circ} CF_3CH_2CF_3.$$

Hydrogen halides also add in a non-catalytic reaction to vinylidene fluoride[32].

In many cases Lewis acids are used as catalysts. For example, hydrogen fluoride adds to $CF_2=CH_2$ and $CF_2=CHCl$ when the reagents are passed through a nickel tube with aluminium trifluoride at 300°.[33] Boron trifluoride has also been successfully used as a catalyst[34]:

$$\begin{matrix} CF_2=CCl_2 \\ CFCl=CFCl \\ CFCl=CCl_2 \\ CHCl=CF_2 \\ CF_3CH=CFCl \end{matrix} \xrightarrow{+HF/BF_3} \begin{matrix} CF_3CHCl_2 \\ CF_3ClCHFCl \\ CF_2ClCHCl_2 \\ CH_2ClCF_3 \\ CF_3CH_2CF_2Cl \end{matrix}$$

1,1-Difluoropropene combines with hydrogen chloride in the presence of aluminium trichloride[35]:

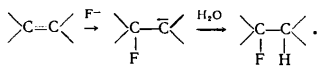
$$CH_3CH=CF_2+HCl \xrightarrow{150^\circ,\ 12\ h} CH_3CH_2CF_2Cl.$$

The addition of hydrogen bromide to hexafluoropropene is catalysed similarly by aluminium tribromide[36].

The addition reactions of hydrogen halides to fluoro-olefins at a high temperature (100–300°) in the presence of activated charcoal impregnated with alkaline earth metal sulphates as catalysts constitute a fairly large group.

Under these conditions hydrogen halides add to perfluoro--olefins in only one way, in conformity with the polarisation of the reactants [37-40]. In all probability the mechanism of these reactions is ionic and it is evident that it can be both electrophilic and nucleophilic. The relative ease of addition to perfluoroisobutene compared with perfluoropropene indicates a nucleophilic mechanism, while an electrophilic mechanism is more likely for fluoro-derivatives of ethylene.

Fluoro-olefins readily combine with hydrogen fluoride under the action of water in the presence of alkali metal fluorides, i.e. by a nucleophilic mechanism [41]:



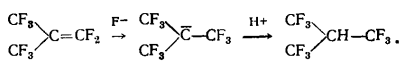
Hydrogen fluoride adds in the same way to trifluoromethyl perfluorovinyl ether [42]:

$$CF_3OCF=CF_2 \xrightarrow{KF} CF_3O\bar{C}FCF_3 \xrightarrow{H_2O} CF_3OCHFCF_3,$$

and to perfluoroallene [43,44]:

$$CF_2=C=CF_2 \xrightarrow{CsF} CF_3\bar{C}=CF_2 \xrightarrow{H_2O} CF_3CH=CF_2.$$

Under nucleophilic reaction conditions the addition of hydrogen fluoride to perfluoroisobutene takes place particularly easily [45,46]:



III. ADDITION OF OTHER INORGANIC ACIDS

Fluorosulphonic acid adds to trifluoroethylene at atmospheric pressure at 20–30° [47]:

$$CFH=CF_2+HOSO_2F \rightarrow CFH_2CF_2O-SO_2F.$$

The adducts of fluorosulphonic acid and vinylidene fluoride and 2-chloro-1,1-difluoroethylene have been obtained under similar conditions [48,49]:

$$CH_2=CF_2+HOSO_2F \rightarrow CH_2CF_2OSO_2F,$$
$$CHCl=CF_2+HOSO_2F \rightarrow CH_2ClCF_2OSO_2F.$$

Perfluoro-olefins require more severe conditions. Thus the addition of fluorosulphonic acid to tetrafluoroethylene, hexafluoropropene, 4-hydroperfluorobut-1-ene, perfluorohept-1-ene, and 8-hydroperfluoro-oct-1-ene requires heating in an autoclave at 150–200° for several hours:

$$R-CF=CF_2+HOSO_2F \rightarrow RCFHCF_2OSO_2F,$$

where R = F, CF_3, $H(CF_2)_2$, $CF_3(CF_2)_4$, and $H(CF_2)_6$.

The addition of sulphuric acid to perfluoropropene requires heating at 350°, which is due to the lower electrophilicity of sulphuric acid compared with fluorosulphonic acid:

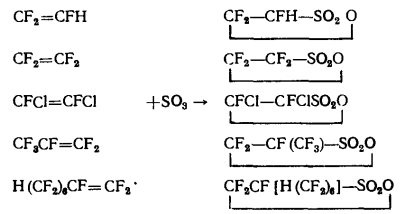
$$CF_3-CF=CF_2+H_2SO_4 \rightarrow CF_3CFHCF_2OSO_3H.$$

In all cases the mode of addition is consistent with the polarisation of the double bond [50,51].

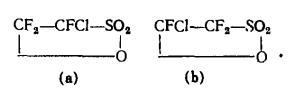
IV. ADDITION OF SULPHUR TRIOXIDE

As already mentioned, fluoro-olefins behave as electron-donor compounds in relation to reagents whose electrophilicity is particularly high. The reaction of fluoro--olefins with sulphur trioxide is a process where this property is particularly marked.

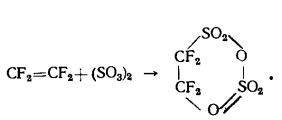
A number of investigators have shown [52-57] that fluoro--olefins readily combine with sulphur trioxide with formation of cyclo-adducts — β-sultones. The initial reaction step is undoubtedly attack on the double bond by the positively charged sulphur atom of sulphur trioxide:



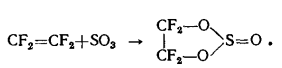
The above examples show that in reactions of asymmetric fluoro-olefins the addition of sulphur trioxide occurs in conformity with the polarisation of the double bond. Contradictory data have been published concerning chlorotrifluoroethylene. Dmitriev et al. [53,55] obtained only one isomer of the addition product, α-chlorotrifluoro-β-sultone (a), formed in conformity with the polarity of the reactants, whereas according to the data of England et al. [56,57] the adduct is a mixture of both possible isomers, (a) and (b):



The experimental conditions of the reactions differed somewhat in the two cases. β-Sultones are the sole reaction products only when freshly-distilled sulphur trioxide (α-form, monomer) is used. The dimer of sulphur trioxide yields pyrosultones:



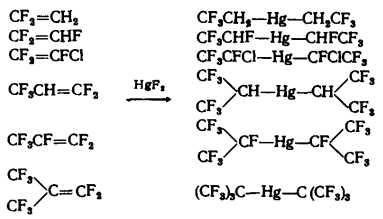
The formation of tetrafluoroethylene sulphite has also been noted [57]:



V. MERCURATION

The fluoro-derivatives of ethylene and higher fluoro--olefins with a terminal double bond combine with mercuric fluoride in solution in arsenic trifluoride or anhydrous hydrogen fluoride (in the latter case mercuric oxide can be used instead of mercuric fluoride). The addition occurs on heating in an autoclave at 50–100° and results in the formation of bis-perfluoroalkyl derivatives of mercury [58-63].

The following series of examples demonstrates the fairly wide range of application of this reaction:

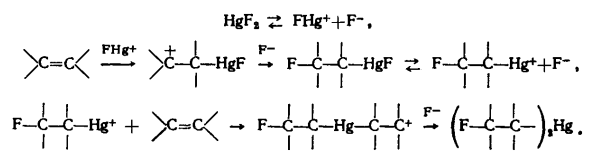


The addition of mercuric fluoride to chlorotrifluoroethylene and tetrafluoroethylene at 100° in an autoclave without solvent leads to small yields of the corresponding perfluoroalkylmercury fluorides[64]:

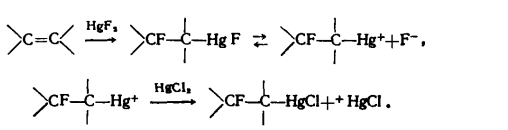
$$CF_2=CFX+HgF_2 \rightarrow CF_2CFX-HgF,$$

where X = F, Cl.

Fluoro-olefins with a non-terminal double bond, such as perfluorocyclobutene and 2,3-dichloro-octafluorobut-2-ene do not combine with mercuric fluoride[65]. There is no doubt that the mechanism of the addition is electrophilic:



This mechanism is confirmed by the fact that undissociated mercuric chloride does not add to fluoro-olefins, while a 1:1 mixture of mercuric fluoride and chloride yields perfluoroalkyl mercury chlorides[62]:

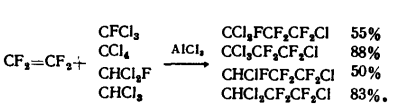


The nucleophilic mechanism of the addition of mercuric fluoride suggested by Goldwhite et al.[64] seems unlikely.

It should be noted that the reaction with mercuric fluoride is the only known example of electrophilic addition to the double bond of perfluoroisobutene. In contrast to other fluoro-olefins, the interaction of $(CF_3)_2C=CF_2$ with mercuric fluoride occurs at 180–200°.[60]

VI. ALKYLATION

In the presence of aluminium chloride, tetrafluoroethylene condenses with chlorotrifluoromethane, carbon tetrachloride, chlorodifluoromethane, and chloroform[66-68]:



The alkylation of asymmetric fluoro-olefins occurs in conformity with the polarity of the double bond. The communication[69] that CCl_3F, CCl_4, $CHFCl_2$, and $CHCl_3$ add to chlorotrifluoroethylene in the presence of aluminium chloride in a manner contrary to the polarity proved to be erroneous[70]. It has been shown that the addition of CCl_4 and $CHCl_3$ to $CF_2=CFCl$ [71,72] also occurs in conformity with the polarisation of the double bond:

$$CF_2=CFCl+CCl_3X \rightarrow CF_2ClCFClCCl_2X,$$

where X = Cl, H. The addition of isopropyl chloride to chlorotrifluoroethylene and the asymmetric dichlorodifluoroethylene in the presence of aluminium chloride has also been described[73]:

$$CF_2=CXCl+(CH_3)_2CHCl \xrightarrow{AlCl_3} CF_2Cl-CXCl-CH(CH_3)_2,$$

where X = F, Cl.

The substitution of fluorine by chlorine and disproportionation are side-processes which usually accompany the reactions of fluoro-olefins in which aluminium chloride participates.

VII. ACYLATION

The addition of the chlorides of carboxylic acids by an electrophilic mechanism in the presence of aluminium chloride (by Kondakov's reaction) was achieved only in the case of vinylidene fluoride and trifluoroethylene[74]. The mode of addition is consistent with the polarity of the starting materials:

$$R-COCl+CF_2=CHX \xrightarrow{AlCl_3} R-CO-CHX-CF_2Cl,$$

where X = H and F and R = CH_3, C_2H_5, and n-C_3H_7.

At the same time there is complete or partial substitution of fluorine by chlorine and products of further condensation are formed. The acylation of perfluoro-olefins can be achieved only by a nucleophilic mechanism. In the presence of alkali metal fluorides, difluorophosgene adds to perfluoro-olefins, yielding the fluorides of perfluoro-carboxylic acids. The fluorides of perfluoro-carboxylic acids react similarly with formation of perfluoro-ketones[75-77]:

$$CF_2=CF_2 \xrightarrow{F^-} CF_3CF_2^- \xrightarrow{COF_2} CF_3-CF_2-COF+F^-,$$
$$CF_3CF_2COF+CF_2=CF_2 \rightarrow CF_3CF_2-CO-CF_2CF_3.$$

VIII. CONDENSATION WITH FORMALDEHYDE

Condensation reactions with formaldehyde in the presence of acid catalysts are characteristic of olefins, and are known to result in the formation of either unsaturated alcohols, or 1,3-glycols or their derivatives — *m*-dioxans. Halogeno-olefins yield β-hydroxy-acids or their derivatives, for example[78]:

$$CCl_2=CCl_2+CH_2O+H_2O \xrightarrow{H^+} [HOCH_2CCl_2CCl_2OH] \xrightarrow{H_2O} HOCH_2CCl_2COOH.$$

The reaction of tetrafluoroethylene with paraformaldehyde in the presence of 80% sulphuric acid in an autoclave at 80°, resulting in a small yield of αα-difluorohydracrylic acid, was described in 1949:[79-81]

$$CF_2=CF_2+CH_2O \rightarrow HOCH_2CF_2COOH.$$

Among other fluoro-olefins only trifluoroethylene reacts with formaldehyde in the presence of 90% sulphuric acid[82]. The product is α-fluorohydracrylic acid:

$$CF_2=CHF+CH_2O \rightarrow HOCH_2CHFCOOH.$$

Catalysts of this reaction which are much more effective than sulphuric acid are chlorosulphonic and fluorosulphonic

acids, in whose presence formaldehyde can be condensed with tetrafluoroethylene, chlorotrifluoroethylene, 1,2-dichloro-1,2-difluoroethylene, and hexafluoropropene[83,84]. In all the cases investigated the following hydracrylic acids were obtained in satisfactory yields:

$CF_2=CF_2$	$HOCH_2CF_2COOH$	62.6%
$CF_3CF=CF_2$	$HOCH_2CFCOOH$ (CF$_3$)	41.3%
$CFCl=CFCl + CH_2O + ClSO_3H \rightarrow$	$HOCH_2CFClCOOH$	50%
$CF_2=CFCl$	$HOCH_2CFClCOOH$	19.8%
	$HOCH_2CF_2COOH$	30.5%

Trifluoroethylene and hexafluoropropene gave respectively α-fluorohydracrylic and α-fluoro-α-trifluoromethylhydracrylic acids which is consistent with the polarity of the double bond in fluoro-olefins. It was to be expected that the condensation of chlorotrifluoroethylene with formaldehyde would give α-chloro-α-fluorohydracrylic acid. This acid was indeed isolated (as the ethyl ester) in 19.8% yield, but the mixture of products also contained 30.5% of the ethyl ester of $\alpha\alpha$-difluorohydracrylic acid whose formation can only be conceived as a result of electrophilic attack on the CF_2 group, i.e. on the carbon atom bearing a positive charge relative to the carbon atom of the CFCl group.

The occurrence of two modes of reaction was also noted for certain other addition reactions of fluoro-olefins, including chlorotrifluoroethylene. However, in this case addition contrary to the polarity is observed for a process about whose ionic character there can not be even the slightest doubt. Apparently this phenomenon can be explained by a competition of steric and polar factors. The effective radius of fluorine is 1.25 Å and of chlorine 1.58 Å; thus the mode of reaction in conformity with the polarisation of the double bond encounters considerable steric hindrance. In nucleophilic addition reactions of chlorotrifluoroethylene the effects of the polar and steric factors reinforce each other and therefore there is strictly only one mode of reaction in such processes.

The condensation of fluoro-olefins with formaldehyde in the presence of fluorosulphonic and chlorosulphonic acids can be represented as follows:

$$ClSO_2{-}OH + CH_2O \rightarrow ClSO_2{-}O{-}CH_2OH \overset{H^+}{\rightleftarrows} ClSO_2OCH_2^+ + H_2O,$$

$$CF_2=CF_2 + ClSO_2OCH_2^+ \rightarrow [ClSO_2OCH_2CF_2CF_2^+] \xrightarrow{ClSO_2O^-}$$
$$\rightarrow ClSO_2OCH_2CF_2CF_2{-}O{-}SO_2Cl \xrightarrow{H_2O} HOCH_2CF_2COOH.$$

The intermediate halogenosulphonates exhibit a high capacity for alkylation, and can therefore be used in the preparation of the corresponding β-halogeno-carboxylic acids[82,83]:

$$FSO_2OCH_2CFClCFCl{-}O{-}SO_2F \xrightarrow{KX,\ H_2O} X{-}CH_2CFClCOOH,$$

where X = Cl and Br.

The study of the condensation of formaldehyde with fluoro-olefins in solution in anhydrous hydrogen fluoride yielded interesting results. Vinylidene fluoride and trifluoroethylene enter into this reaction even at 0°, the products being fluorinated ethers[85-87]:

$$CF_2=CH_2 + CH_2O + HF \rightarrow CF_3CH_2CH_2{-}O{-}CH_2CH_2CF_3,$$

$$CF_2=CHF + CH_2O + HF \rightarrow CF_3CHFCH_2{-}O{-}CH_2CHFCF_3.$$

The condensation in the presence of alcohols gives the corresponding mixed ethers[88,89] and in the presence of acetic acid the products are fluoroalkyl acetates[89]:

$$CF_2=CH_2 + CH_2O + HF + ROH \rightarrow CF_3CH_2CH_2{-}O{-}R,$$

$$CF_2=CH_2 + CH_2O + HF + CH_3COOH \rightarrow CH_3COOCH_2CH_2CF_3.$$

In the reaction with trifluoroethylene, the alcohol CF_3CFHCH_2OH is formed together with the ether $(CF_3CFHCH_2)_2O$. Alcohols or their fluoromethyl ethers are the main products of the condensation of the aldehyde with the perfluoro-olefins tetrafluoroethylene and hexafluoropropene[87,90,91]:

$$RCF=CF_2 + CH_2O + HF \rightarrow RCF_2CF_2CH_2OH + RCF_2CF_2CH_2{-}O{-}CH_2F,$$

where R = F and CF_3.

There are data[87] showing that a solution of paraformaldehyde in anhydrous hydrogen fluoride is an equilibrium mixture consisting of 25–30% of fluoromethanol and 70–75% of fluoromethyl ether:

$$CH_2=O + HF \rightleftarrows FCH_2OH + FCH_2{-}O{-}CH_2F.$$

The formation of all the products of the formaldehyde condensations of fluoro-olefins in solution in hydrogen fluoride can be satisfactorily explained by postulating dissociation of these compounds at the C–F bond:

$$FCH_2OH \rightleftarrows {}^+CH_2OH + F^-,$$

$$FCH_2OCH_2F \rightleftarrows FCH_2OCH_2^+ + F^-,$$

$$CF_2=CFH \xrightarrow{HOCH_2^+} [{}^+CF_2CFHCH_2OH] \xrightarrow{F^-} CF_3CHFCH_2OH,$$
$$\downarrow FCH_2OCH_2^+$$
$$[{}^+CF_2{-}CFH{-}CH_2OCH_2F] \xrightarrow{F^-} CF_3CFHCH_2OCH_2F \xrightarrow{-F^-}$$
$$\rightarrow [CF_3CFHCH_2OCH_2^+] \xrightarrow{CF_2=CFH} [CF_3CFHCH_2OCH_2CFHCF_2^+] \xrightarrow{F^-} (CF_3CFHCH_2)_2O$$

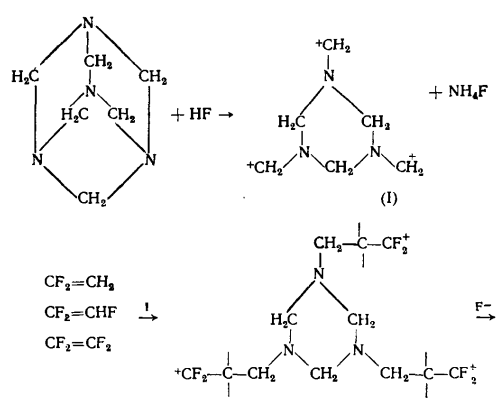
The participation of fluoromethyl ether in these reactions is not essential; under the action of the hydroxymethyl cation alone the same results are obtained:

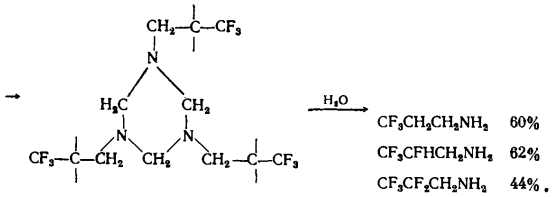
$$CF_2=CFH \xrightarrow{HOCH_2^+} CF_3CFHCH_2OH \xrightarrow{CH_2O} [CF_3CFHCH_2OCH_2OH] \xrightarrow{H^+}$$
$$\rightarrow [CF_3CFHCH_2OCH_2^+] \xrightarrow{CF_2=CFH} [CF_3CFHCH_2OCH_2CFHCF_2^+] \xrightarrow{F^-}$$
$$\rightarrow CF_3CFHCH_2OCH_2CFHCF_3, \text{ etc.}$$

It is interesting that a cyclodimer has also been isolated from the products of the reaction of tetrafluoroethylene with formaldehyde in hydrogen fluoride[87]:

$$\begin{matrix} CF_2=CF_2 \\ CH_2=O \end{matrix} \rightarrow \begin{matrix} CF_2{-}CF_2 \\ | \quad | \\ CH_2{-}O \end{matrix}.$$

In the reaction of fluoro-olefins with a solution of hexamethylenetetramine in hydrogen fluoride aminomethylation takes place[92]:





IX. NITRATION

The nitration of fluoro-olefins can be achieved both by radical and ionic mechanisms. In the radical process, the nitrating agent is the monomer of nitrogen dioxide, the reaction products being vicinal dinitro-compounds and nitro-nitrites whose hydrolysis leads to fluorine-containing nitro-acids, nitro-ketones, or nitro-alcohols[93-100]. On the other hand, in ionic processes various nitrating agents are used, forming the nitronium cation under the reaction conditions. One of the best investigated reactions of this type is the nitrofluorination of fluoro-olefins with a mixture of nitric acid and anhydrous hydrogen fluoride:

$$HNO_3 + HF \rightleftarrows O_2N^+ + 2F^- + H_3O^+$$

$$>C=C< + O_2N^+ \rightarrow \left[>C-\overset{+}{C}<\right] \xrightarrow{F^-} >C-C<$$
$$\qquad\qquad\qquad\quad NO_2 \qquad\qquad NO_2\ F$$

In the fluoro-olefin series this reaction was first achieved for tetrafluoroethylene[101]:

$$CF_2=CF_2 + HNO_3 + HF \rightarrow CF_3CF_2NO_2.$$

The study of the nitrofluorination of asymmetric fluoro-olefins[102,103] showed that the mode of addition is determined by the polarity of the double bond:

$CF_2=CH_2$	$CF_3CH_2NO_2$	59%
$CF_2=CHF$	CF_3CFHNO_2	86%
$CF_2=CFCl$ + HNO_3/HF →	$CF_3CFClNO_2$	88%
$CF_2=CFCF_3$	$(CF_3)_2CFNO_2$	75%.

The hydrogen-containing fluoro-olefins vinylidene fluoride and trifluoroethylene are most readily nitrofluorinated. They react when bubbled through a mixture of anhydrous hydrogen fluoride and nitric acid at -60°. Tetrafluoroethylene and chlorotrifluoroethylene react at 10–20°[102] and hexafluoropropene on heating in an autoclave at 60°.[103]

The nitration of fluoro-olefins with a mixture of nitric and sulphuric acids has also been investigated. The products are fluoronitro-carboxylic acids or their chlorides[104]. The reaction mechanism is ionic, involving attack by the nitronium cation on the double bond. Thus the action of sulphuric and nitric acids on tetrafluoroethylene and chlorotrifluoroethylene results in the formation of difluoronitroacetic acid[105]:

$$\begin{matrix}CF_2=CF_2\\CF_2=CFCl\end{matrix} + HNO_3/H_2SO_4 \rightarrow CF_2NO_2COOH.$$

Similarly symmetrical dichlorodifluoroethylene gives chlorofluoronitroacetic acid[106]:

$$CFCl=CFCl \rightarrow CFClNO_2COOH,$$

and 2,2-dichloro-1-fluoroethylene gives the chloride of fluoronitroacetic acid[107]:

$$CCl_2=CHF \rightarrow CHFNO_2COCl.$$

The perhalogenopropenes $(CF_2Cl)CCl=CCl_2$ and $CF_3CCl=CCl_2$ yield the acid chlorides $(CF_3Cl)CClNO_2COCl$ and CF_3CClNO_2COCl respectively[108].

The possibility of using nitryl fluoride as the nitrating agent has been almost not investigated. However, it has been shown that NO_2F adds to the double bonds of alkyl perfluorovinyl ethers with the formation of fluorinated nitro-ethers which can be converted into esters of perfluoronitro-carboxylic acids[109]. The esters of tetrafluoro--α-nitropropionic and hexafluoro-α-nitroisobutyric acids were obtained in this way:

$$CF_3-C(R)=CF-OR' + FNO_2 \rightarrow CF_3-C(R)(NO_2)-CF_2-OR' \xrightarrow{AlCl_3}$$
$$\rightarrow CF_3-C(R)(NO_2)-C(=O)X \xrightarrow{R'OH} CF_3-C(R)(NO_2)-COOR',$$

where R = F and CF_3, X = F or Cl, and R′ = alkyl.

X. NITROSATION

The nitrosation of fluoro-olefins, i.e. the addition of various nitrosating agents to the double bond, for example nitrosyl halides or nitrogen oxides, is of considerable interest as a possible general pathway for the synthesis of fluoronitroso-alkanes and fluoronitroso-compounds with different functional groups. These reactions can be divided into two groups. The first group comprises the homolytic processes

$$>C=C< \xrightarrow{X^\cdot} X-C-\underset{A}{C}\cdot \xrightarrow{NO} X-C-C-NO.$$

The radical X′ attacks the double bond of the fluoro-olefins, the intermediate radical A being stabilised by the addition of the radical-like molecule of nitric oxide. Dinitrogen trioxide[110] and nitrosyl chloride[111,112] add to fluoro-olefins in this way. The second group of reactions includes processes for which a heterolytic mechanism has been demonstrated or is at least likely. These reactions are discussed regardless of whether they yield nitroso-compounds or products of further reactions of the latter.

Nitrosyl chloride reacts with tetrafluoroethylene, chlorotrifluoroethylene, and asymmetric dichlorodifluoroethylene when the mixture is passed through a heated Pyrex tube, the products being nitro-compounds[113]:

$$CF_2=CF_2 \xrightarrow{50^\circ} CF_2ClCF_2NO_2, \qquad 63\%$$
$$CF_2=CFCl + NOCl \xrightarrow{100^\circ} CF_2ClCFClNO_2, \qquad 67\%$$
$$CF_2=CCl_2 \xrightarrow{100^\circ} CF_2ClCCl_2NO_2. \qquad 57\%$$

Similar results are obtained when the reaction is carried out in sealed tubes[114,115] or in an autoclave[116] at room temperature; thus $CF_2=CFCl$ forms a nitro-compound and 1,2,2-trichloro-1,1,2-trifluoroethane:

$$CF_2=CFCl + NOCl \rightarrow CF_2ClCFClNO_2 + {}^1/_2\,Cl_2 + {}^1/_2\,N_2.$$
$$\xrightarrow{Cl_2} CF_2ClCFCl_2$$

When the initially formed nitroso-compound contains a hydrogen atom in the α position, it is stabilised by the nitroso-oxime rearrangement, for example[114,115]:

$$CHF=CHCl + NOCl \rightarrow [CHFClCHClNO] \rightarrow CHFCl-CCl=NOH.$$

It is readily seen that in all the cases quoted above the addition of nitrosyl chloride occurs in conformity with the

polarisation of the double bond. Nitrosyl bromide and tetrafluoroethylene react in an autoclave at 55° to give $O_2NCF_2CF_2Br$.[113] The intermediate formation of nitroso--compounds is confirmed by the fact that in the reaction of nitrosyl chloride with an excess of $CF_2=CF_2$ in an autoclave at 100° the principal product is oxazetidine[116]:

$$CF_2=CF_2 + ClNO \rightarrow ClCF_2-CF_2-N=O \xrightarrow{CF_2=CF_2} CF_2ClCF_2-N(-O)-CF_2-CF_2 .$$

It has been established that the addition of nitrosyl chloride to tetrafluoroethylene in the liquid phase can occur by an ionic electrophilic mechanism. The reaction occurs smoothly on bubbling $CF_2=CF_2$ through a solution of aluminium trichloride in nitrosyl chloride at -78°.[117] When nitrosyl chloride was added to $CF_2=CF_2$ and $CF_2=CFCl$ in a tube over ferric chloride at 45°, nitroso-compounds, dichlorides, and chloronitro- and dinitro-compounds were isolated[118], the yield of the nitroso-compounds being of the order of 80%. Similar results were obtained when nitric oxide was used instead of nitrosyl chloride[119]. The authors of these studies believe that in the latter case the first reaction step is the formation of nitrosyl chloride from nitric oxide and ferric chloride:

$$NO + FeCl_3 \rightleftarrows NOFeCl_3,$$
$$NOFeCl_4 + NO \rightarrow NOFeCl_2 + NOCl,$$
$$NOCl + FeCl_3 \rightarrow NOFeCl_4,$$
$$NOFeCl_4 + 2\,NO \rightarrow NOFeCl_2 + 2\,NOCl,$$

although usually these processes occur at a higher temperature than the one at which the NO + $FeCl_3$ mixture interacts with fluoro-olefins.

The authors believe that the addition of nitrosyl chloride to fluoro-olefins over ferric chloride takes place by a radical mechanism. They base this view on the idea, prevalent until recently, that fluoro-olefins are incapable of undergoing electrophilic addition reactions. However, as already mentioned, numerous studies in recent years showed that fluoro-olefins have by no means lost the electron-donor properties characteristic of olefins and under certain conditions enter into electrophilic reactions. Comparison with the results obtained by Titov[117] suggests that the mechanism of these reactions is similar and can be represented as follows:

$$NOCl + MCl_3 \rightleftarrows NO^+ + MCl_4^-$$
$$CF_2=CF_2 + {}^+NO \rightarrow [CF_2(NO)-CF_2^+] \xrightarrow{MCl_4^-} CF_2(NO)-CF_2Cl + MCl_3$$

where M = Al, and Fe.

There is no doubt that the addition of nitrosyl chloride to alkyl perfluorovinyl ethers has an electrophilic mechanism[120]:

$$\begin{matrix} CF_2=CF-OR \\ ClCF=CF-OR \\ CF_3CF=CFOR \end{matrix} + NOCl \xrightarrow{-78°} \begin{matrix} ON-CF_2CFClOR \\ ON-CFClCFClOR, \\ CF_2CFCFClOR \\ | \\ NO \end{matrix}$$

where R = CH_3, and C_2H_5.

As mentioned in Section IX, nitrogen dioxide reacts with fluoro-olefins by a radical mechanism with formation of dinitro-compounds and nitro-nitrites. The interaction of nitrogen dioxide with alkyl perfluorovinyl ethers[121], resulting after hydrolysis in the formation of fluoro-α--nitroso-carboxylic acid esters, is of a quite different type:

$$X-CF=CFOR + N_2O_4 \xrightarrow{-78°} [XCF(NO)-CF(ONO_2)-OR] \xrightarrow{H_2O} XCF(NO)-COOR,$$

where X = F, Cl, and CF_3 and R = CH_3 and C_2H_5.

The esters of difluoronitrosoacetic acid $ONCF_2COOR$, chlorofluoronitrosoacetic acid ONCFClCOOR, and tetrafluoro-α-nitrosopropionic acid $CF_3CF(NO)COOR$ have been prepared in this way. The dimer of nitrogen dioxide enters into this reaction as nitrosonium nitrate:

$$N_2O_4 \rightleftarrows {}^+NO + {}^-ONO_2.$$

The conjugation with the unshared electron pair of the oxygen atoms makes the double bond of the alkyl perfluorovinyl ethers sufficiently nucleophilic for reaction with dinitrogen tetroxide by an ionic mechanism.

The addition of nitrosyl fluoride to fluoro-olefins was first achieved by Knunyants et al.[122], who studied the interaction of nitrosyl fluoride with $CH_2=CF_2$, $CHF=CF_2$, $CF_2=CF_2$, $CF_2=CFCF_3$, and $CF_2=C(CF_3)_2$. It was found that the addition of nitrosyl fluoride to perfluoroisobutene proceeds smoothly at room temperature in an autoclave in the presence of a small amount of potassium fluoride with formation of nonafluoronitroso-t-butane:

$$(CF_3)_2C=CF_2 + NOF \rightarrow (CF_3)_3CNO.$$

Perfluoropropene reacts with nitrosyl fluoride on heating at 150° in the presence of calcium sulphate on activated charcoal as the catalyst. Heptafluoro-2-nitrosopropane $(CF_3)_2CFNO$ is obtained in a small yield; the main products are substances formed as a result of its further reaction — hexafluoroisopropyl nitrite $(CF_3)_2CF(ONO)$ and hexafluoroacetone CF_3COCF_3 — and also as a result of side--processes of a radical type — hexafluoronitronitrosopropane $CF_3CF(NO)CF_2NO_2$, the hydrate of pentafluoronitroacetone $CF_3C(OH)_2CF_2NO_2$, etc. In the absence of a catalyst products of the radical nitration of $CF_3CF=CF_2$ are formed exclusively. In the presence of $CaSO_4/C$ tetrafluoroethylene reacts with nitrosyl fluoride at 70–80°, the main product being the corresponding oxazetidine:

$$CF_2=CF_2 + NOF \rightarrow CF_3CF_2-N=O \xrightarrow{CF_2=CF_2} CF_3CF_2-N(-O)-CF_2-CF_2 .$$

Trifluoroethylene and vinylidene fluoride react with nitrosyl fluoride very readily at room temperature without catalyst in an inert solvent. Reaction with $CF_2=CFH$ gave CF_3CF_2NO,

$$CF_2=CFH + NOF \rightarrow [CF_2(NO)CFHF] \rightarrow [CF_2=CF(NO)H] \xrightarrow{HF} \rightarrow [CF_2(NO)CF_2H(OH)] \xrightarrow{[O]} CF_3CF_2NO.$$

and reaction with $CF_2=CH_2$ gave a compound to which the following structure was attributed:

$$CF_3CF_2N(-O)-CF_2-CH(-OH)-N-.$$

The results of Knunyants and coworkers were subsequently confirmed by Andreades[123], who showed that the addition of nitrosyl fluoride to $CF_2=C(CF_3)_2$ occurs readily even without catalyst. Perfluorobut-2-ene, an olefin with a central double bond, proved to be incapable of combining with nitrosyl fluoride even at a high temperature (200°),

yielding only degradation products — CF_3COF, $CF_3CF_2NO_2$, CF_3NO_2, CF_3CF_2COF, etc.[123]

The addition of nitrosyl fluoride to alkyl perfluorovinyl ethers proceeds exceptionally easily (at -78°)[120]:

$$\begin{matrix} CF_2{=}CF{-}OR \\ CFCl{=}CFOR \\ CF_3CF{=}CFOR \end{matrix} + NOF \rightarrow \begin{matrix} ONCF_2CF_2OR \\ ONCFClCF_2OR \\ CF_3CF(NO)CF_2OR \end{matrix},$$

where R = CH_3 or C_2H_5. However, the addition of nitrosyl fluoride to ethyl perfluoroisobutenyl ether occurs only at room temperature:

$$\begin{matrix} CF_3 \\ CF_3 \end{matrix}\!\!>\!C{=}CF{-}OC_2H_5 \xrightarrow{NOF} \begin{matrix} CF_3 \\ CF_3 \end{matrix}\!\!>\!C(NO){-}CF_2OC_2H_5.$$

Nitrosyl fluoride adds very readily to the fluoride of perfluoromethacrylic acid $CF_2{=}C(CF_3)COF$ and di(trifluoromethyl)keten $(CF_3)_2C{=}C{=}O$ [124] which are distinguished by exceptionally high electrophilicity. An examination of the above addition reactions of nitrosyl fluoride at the double bond readily reveals an interesting peculiarity consisting of the fact that the addition takes place easily to vinyl ethers and hydrogen-containing fluoroethylenes ($CH_2{=}CF_2$ and $CHF{=}CF_2$), becomes more difficult with $CF_2{=}CF_2$ and $CF_2{=}CF{-}CF_3$, and then again becomes very much easier with $(CF_3)_2C{=}CF_2$. This behaviour has the following logical explanation. The addition to vinyl ethers and the first members of the fluoro-olefin series involves an electrophilic mechanism and begins with attack by the nitrosonium cation; while in the addition of perfluoroisobutene, nitrosyl fluoride behaves as a nucleophilic agent and the first reaction step is attack on the double bond by the fluoride anion:

$$NOF \rightleftarrows F^- + \overset{+}{N}O,$$

$$CF_2{=}CF{-}OR \xrightarrow{+NO} [ON{-}CF_2{-}\overset{+}{C}FOR] \xrightarrow{F^-} ONCF_2CF_2OR,$$

$$F_3C{\equiv}C{-}C{=}C_2 \xrightarrow{F^-} [(CF_3)_3C^-] \xrightarrow{+NO} (CF_3)_3C{-}NO.$$

The nucleophilic mechanism of the addition of nitrosyl fluoride to higher fluoro-olefins was confirmed by the experimental finding[125] that alkali metal fluorides are effective catalysts of the addition reaction, particularly in strongly ionising solvents. Thus interaction of nitrosyl fluoride with perfluoropropene and perfluorocyclobutene in sulpholane in the presence of potassium fluoride and caesium fluoride gives the corresponding nitroso-compounds in yields of the order of 70%:

$$\begin{matrix} CF_3CF{=}CF_2 \\ CF_2{-}CF \\ CF_2{-}CF \end{matrix} + NOF \rightarrow \begin{matrix} CF_3CF(NO)CF_3 \\ CF_2{-}CF{-}NO \\ CF_2{-}CF_2 \end{matrix}.$$

Potassium and caesium fluorides do not catalyse the reaction of nitrosyl fluoride with $CF_2{=}CF_2$ and $CF_2{=}CFCl$ in sulpholane; on the other hand, in the presence of Lewis acids, for example boron trifluoride, in sulpholane, the reaction mixture reacts under mild conditions, and in the case of $CF_2{=}CFCl$ it is possible to isolate in 30% yield α-chlorotetrafluoronitrosoethane $CF_3CFClNO$, whose formation is consistent with the polarity of the reactants[126]. In addition to the nitroso-alkane, a non-distillable oil is formed, probably a copolymer of $CF_3CFClNO$ and $CF_2{=}CFCl$. Only traces of $CF_3{-}CF_2NO$ can be obtained from $CF_2{=}CF_2$, the main reaction product being the copolymer of the two compounds.

Thus there is a reversal of the mechanism of the addition of nitrosyl fluoride in the following series: $CF_2{=}CF{-}O{-}R$; $CF_2{=}CH_2$; $CF_2{=}CHF$; $CF_2{=}CFCl$; $CF_2{=}CF_2$; $CF_2{=}CFCF_3$; $(CF_3)_2C{=}CF_2$; $CF_2{=}C(CF_3)COF$; $(CF_3)_2C{=}C{=}O$. The addition of nitrosyl fluoride to first members of this series, including tetrafluoroethylene, proceeds by an eletrophilic mechanism, and, starting with perfluoropropene, by a nucleophilic mechanism. The present review shows that a similar reversal of mechanism occurs also for a number of other reactions of fluoro-olefins but the present case is particularly interesting, since here we are dealing with the reversal of the mechanism of the addition of the same reagent.

A complete analogy can be drawn with the addition of hydrogen fluoride to fluoro-olefins discussed in Section II:

$$HF \rightleftarrows H^+ + F^-,$$

$$CF_2{=}CH_2 \xrightarrow{H^+} [CH_3CF_2^+] \xrightarrow{F^-} CH_3CF_3,$$

$$\begin{matrix} CF_3 \\ CF_3 \end{matrix}\!\!>\!C{=}CF_2 \xrightarrow{F^+} \left[\begin{matrix} CF_3 \\ CF_3 \end{matrix}\!\!>\!\overset{-}{C}{-}CF_3\right] \xrightarrow{H^+} (CF_3)_3CH.$$

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THE PART PLAYED BY STRUCTURAL PHENOMENA IN DETERMINING THE PROPERTIES OF POLYMERS†

V.A.Kargin

We have all been accustomed to relating the properties of polymers in the first place to the chemical composition, structure, and dimensions of their molecules. The detection of structural formations in a wide variety of polymers, however, is making it necessary to devote increasing attention not only to the actual molecules of the polymers but also to their mutual arrangement and packing. The part played by these structural formations in determining the properties of polymers is often as great as in the case of metals, silicates, and other solids.

Despite the very great variety of morphological forms, it is now possible to distinguish the chief types of structural formation in polymers, in both crystalline and amorphous states.

The simplest type consists of the globular structures, formed by one or many polymer molecules, coiled up into spherical particles. This type of structure is characteristic of amorphous polymers in the vitreous state, although almost any polymer can be obtained in the form of amorphous globules. The formation of globules is accompanied by the loss of an appreciable number of the properties characteristic of linear molecules, and globular polymers are generally brittle and are broken by mechanical shock. Globular structures may also be present, infrequently, in elastic polymers. In this case the globules uncoil on deformation, and the polymers exhibit elastic properties, but have a reduced strength. Thus this type of structure does not favour good mechanical properties. Typical globular structures for polyacrylic acid, polyvinyl chloride, and fluorocarbon rubber are shown in Fig.1. The mechanism of formation of these structures

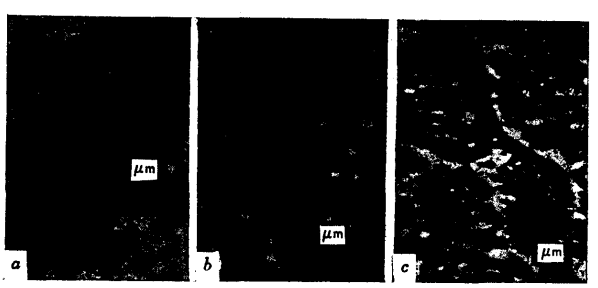

Fig.1. Globular structures: *a*) polyacrylic acid; *b*) polyvinyl chloride; *c*) SKF-26 fluorocarbon rubber.

† Paper presented at the International Symposium on the Chemistry of Macromolecules, Prague, 1965.

was the subject of a paper presented at the Symposium on Polymers in Wiesbaden and has been described in a number of papers[1-7].

Increased rigidity of the molecular chains or decreased intramolecular interaction produces a type of structure consisting of straight chains, which are, however, aggregated into bundles. These structural formations consist of tens or hundreds of chains and are the simplest structural units from which all subsequent types of structure are formed. In amorphous glasses, long thin bundles of chains may be formed, and these, as a result of subsequent aggregation, may form dendrites with regular shapes and very large dimensions of several hundred microns. This type of linear amorphous structure is illustrated in Fig. 2, which shows the sodium salt of polyacrylic acid and the bundles and dendrites of the copolymer formed by acrylic acid and diethyl vinylphosphonate[2,8].

In the elastic state in amorphous polymers, another very typical type of structure is produced — banded structures consisting of formations which now have much greater dimensions. These structures are characteristic of almost any polymer in the elastic state, but because of experimental difficulties they were detected only comparatively recently. Fig. 3 gives as examples the structures of natural rubber in the amorphous state, the copolymer of butadiene and styrene, and vinyl octanoate[9-11]. These banded structures are apparently secondary formations. When specimens are prepared for electron-microscope study at very low temperatures or in the initial stages of crystallisation, it is also possible to see the formation of the simplest fibrillar structures in rubbers (Fig. 4).

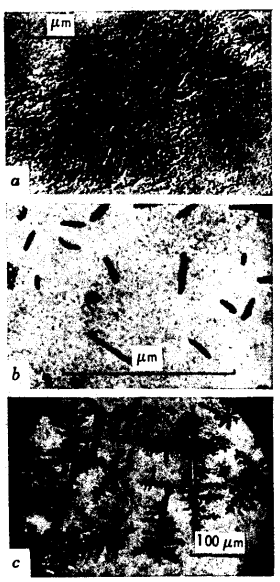

Fig. 2. Fibrillar structures of amorphous polymers:
a) rods formed by the sodium salt of polyacrylic acid; *b*) bundles formed by the copolymer of acrylic acid and diethyl vinylphosphonate; *c*) dendrites of the same copolymer.

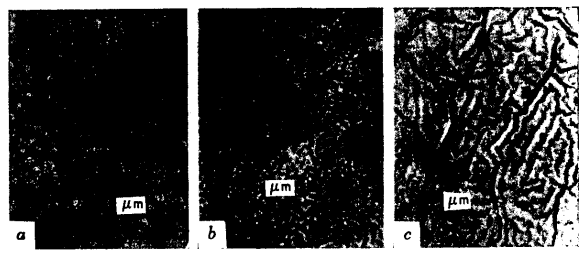

Fig. 3. Banded structures:
a) natural rubber; *b*) butadiene–styrene rubber; *c*) vinyl octanoate.

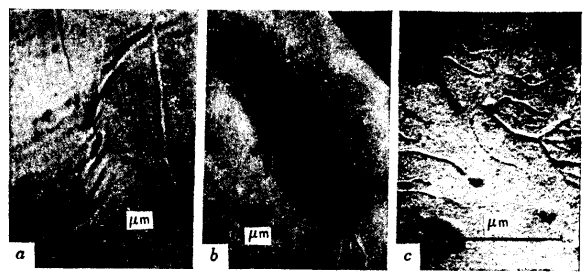

Fig. 4. Simplest fibrillar structures in rubbers, produced by crystallisaton (*a* and *b*) and at low temperatures (*c*).

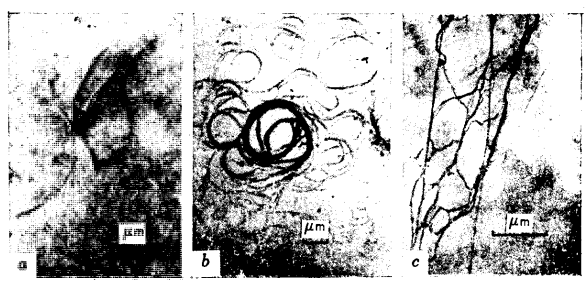

Fig. 5. Bundle-like structures in crystalline polymers:
a) polypropylene; *b*) polyamide copolymer; *c*) polyethylene.

As in amorphous polymers, the simplest structural formations in crystalline polymers are bundles of chains. Fig. 5 gives examples of such formations in polypropylene and a polyamide–polyethylene copolymer[12]. Further combination to give more complex formations may take place by two different mechanisms: the formations may combine by the familiar mechanism first discovered by Keller[13], to give planes which form spherulites and single crystals, or they may combine to give larger linear formations or fibrils which undergo further aggregation, again with the formation of spherulites and single crystals. Fig. 6 shows typical spherulites and crystals of lamellar type formed by isotactic polystyrene[14]. Formations of this type given by polystyrene have been well studied. Typical fibrillar formations are also illustrated in Fig. 7, which shows spherulites and crystals of polypropylene[15].

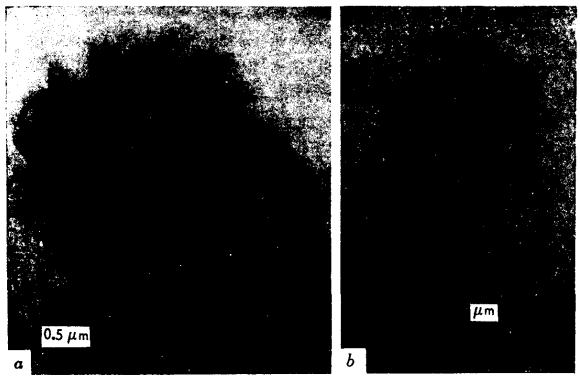

Fig. 6. Spherulite (*a*) and crystals (*b*) of the lamellar type of isotactic polystyrene.

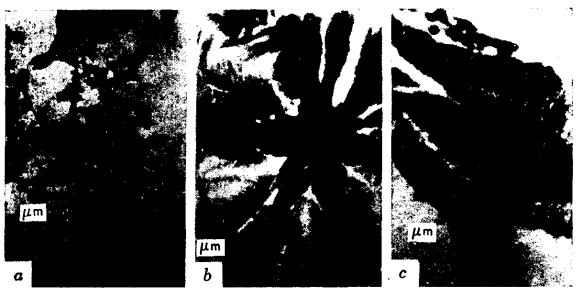

Fig. 7. Spherulites (*a* and *b*) and crystals (*c*) of polypropylene with fibrillar structure.

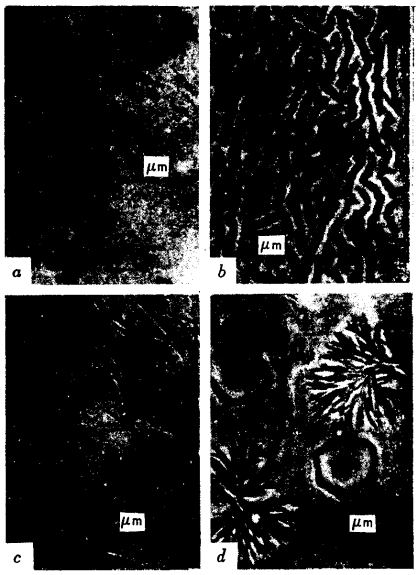

Fig. 8. The four basic structural forms observed in polymers:
a) globular structures of polyacrylic acid; *b*) banded structures in amorphous butadiene–styrene rubber; *c*) fibrillar structures of polypropylene; *d*) spherulites and crystals of isotactic polybutylene.

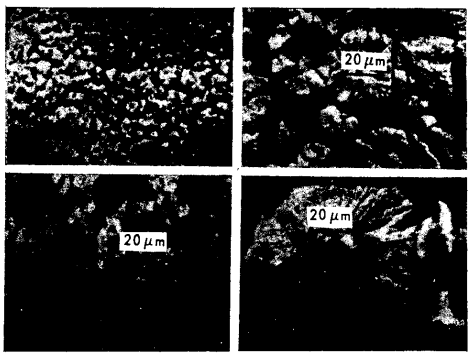

Fig. 9. Spherulitic structures of various dimensions in gutta-percha.

Thus among the great variety of structural forms in polymers, it is possible to distinguish clearly four basic types of structure: globular structures, usually produced in amorphous polymers obtained by polycondensation; banded structures, typical of all polymers in the elastic state (rubbers); fibrillar structures, characteristic of extensively ordered amorphous addition polymers and the initial stages of crystallisation; and finally the large structural formations in crystalline polymers — spherulites and crystals. The four characteristic types of polymer structure are illustrated in Fig. 8.[16]

It can now be confidently stated that the formation of globular and coarsely-crystalline structures has an unfavourable influence on the production of satisfactory mechanical properties. The coiling of linear chains into globules usually leads to the loss of elastic properties, and the mechanical heterogeneity of coarsely-crystalline polymers leads to the ready formation of cracks and to premature breakdown. The formation of simple fibrillar structures is always favourable. Banded structures have as yet been little studied, but they apparently occupy an intermediate position. Thus decrease in the dimensions of coarsely-crystalline formations and uncoiling of globules with conversion into linear formations should lead to an improvement in mechanical properties. The influence of the dimensions of the crystalline formations can be illustrated for the case of gutta-percha. The dimensions of the spherulites produced can be readily altered by altering the thermal conditions of crystallisation. Fig. 9 shows photomicrographs for gutta-percha specimens with spherulites of different dimensions, and Fig. 10 shows stress–tensile strain plots for the same specimens. It can be seen that merely by decreasing the dimensions of the spherulites it is possible to increase the tensile strength and elongation on rupture several times over[17-20].

By altering the conditions of the preparation, Slonimskii[21] was able to convert the globular form of the polyester of isophthalic acid and phenolphthalein into a fibrillar form, with a corresponding marked change in the mechanical properties. Fig. 11 and the Table give respectively

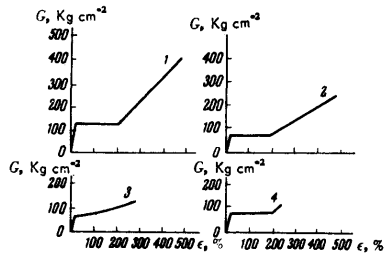

Fig. 10. Stress–tensile strain relations for the gutta-percha specimens whose structures are shown in Fig. 9.

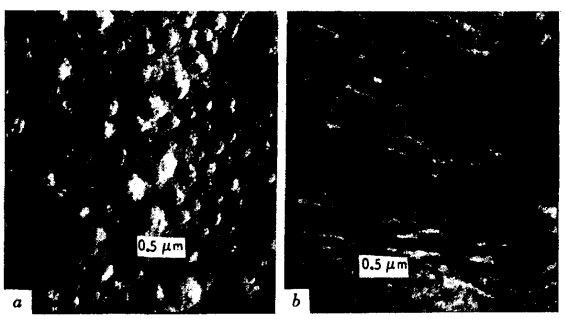

Fig. 11. Globular (*a*) and fibrillar (*b*) structures of the polyester formed by isophthalic acid and phenolphthalein.

TABLE. Properties of the polyester formed by isophthalic acid and phenolphthalein, with globular and fibrillar structures.

Property	Globular	Fibrillar	Property	Globular	Fibrillar
Molecular weight	28 000	28 000	Elongation at rupture, %	10—20	50—80
Softening temperature, °C	270	290	Specific impact strength,		
Tensile strength, Kg cm^{-2}	640	740	Kg cm cm^{-2}	2—3	6—10

photomicrographs of the structures and the mechanical characteristics of the linear and globular polyesters. These examples show that structure may have a considerable influence on mechanical properties and that it is important to be able to control the structure[17-21].

The simplest problem in this field is possibly the control of the dimensions of the coarsely-crystalline formations or spherulites. Spherulitic structures are typical of most readily-crystallising polymers, and there are now several examples of control of this type. Firstly, we have the introduction of synthetic crystallisation nuclei, which act as centres for the formation of spherulites. The greater the quantity of such centres introduced, the smaller will be the dimensions of each spherulite. The dimensions of the spherulites can also be altered by thermal treatment of melts to alter the number of natural nuclei. In this case, however, recrystallisation phenomena with consequent aging of the polymer material are possible. Synthetic nuclei make it possible not only to alter the dimensions of structural formations, but also to preserve them, with a consequent increase in the stability of the material[22-25].

As an example of the action of synthetic nuclei, Figs. 12 and 13 give respectively the structures and deformation curves for pure isotactic polystyrene and for polystyrene containing indigo particles to act as nuclei. Analogous behaviour is shown by many and possibly all crystallising polymers capable of forming structures having large dimensions[24].

It is also possible to alter the dimensions of the structural formations, and hence the properties, by introducing low-molecular compounds, which act as surface-active

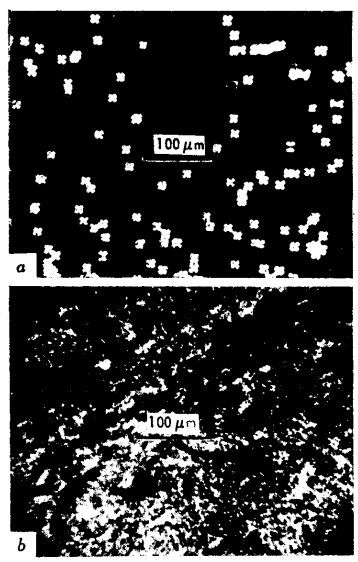

Fig. 12. Structure of specimens of isotactic polystyrene: *a*) pure; *b*) containing indigo.

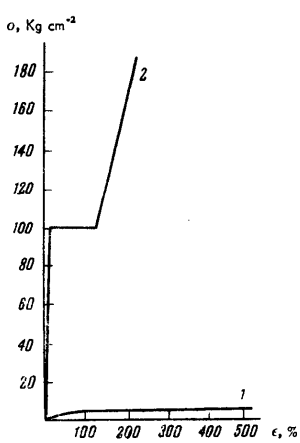

Fig. 13. Deformation curves for the elongation of specimens at 110°:
1) pure isotactic polystyrene; 2) isotactic polystyrene containing indigo.

substances. These are sorbed on the surface of the structural formations, and the dimensions and shapes of the latter are altered in a fashion analogous to that familiar for crystals of low-molecular substances. Fig. 14 gives photographs of the spherulites for nylon 66 with and without the addition of 1,4-dimesidinoanthraquinone. We see again the sharp change in structure, again accompanied by a change in properties[26]. It must be remembered, however, that low-molecular substances introduced into crystalline polymers may produce a quite different effect, particularly when added in comparatively large quantities. By distributing themselves over the interfaces between the simplest structural formations, for example bundles of chains or fibrils, they increase the mobility of the latter and lead to the development of brittle structures. Fig. 15 shows photographs of the structures of pure isotactic polystyrene and polystyrene containing 20 vol.% of cetyl chloride.

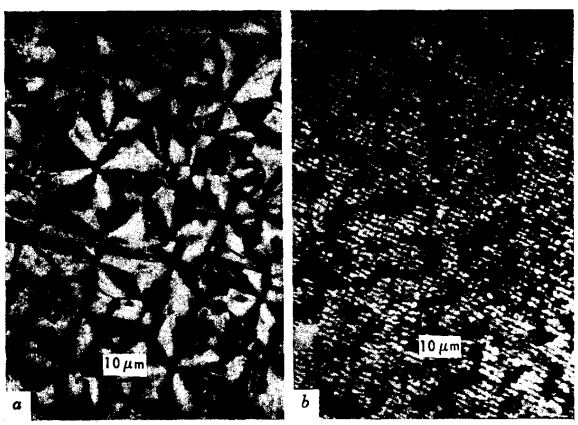

Fig. 14. Structure of nylon 66: *a*) pure; *b*) containing 1,4-dimesidinoanthraquinone.

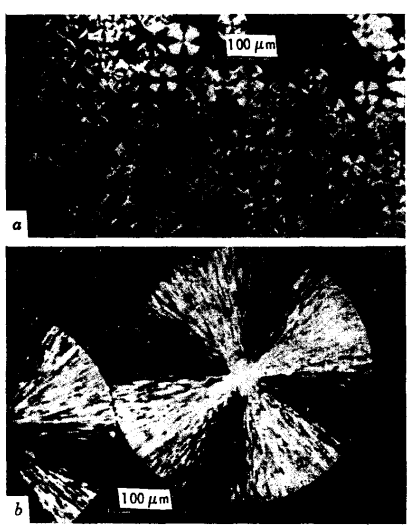

Fig. 15. Structure of isotactic polystyrene: *a*) pure; *b*) containing cetyl chloride.

Brittle spherulites are produced and the specimen becomes weak and brittle. This is why attempts to plasticise crystalline polymers by means of the usual plasticising agents often leads to the opposite of the expected results — the production of brittleness in the specimens being plasticised[27].

Mention may be made of the grafting of polymers as a means of controlling structures; this was described at the previous symposium in Paris[28]. The grafting of any other polymer generally hinders the formation of higher structures, whereas it does not prevent the development of simpler structures, more favourable for the production of the required mechanical properties. We shall not consider this question in more detail.

Up to the present we have dealt only with physical methods for influencing structure formation processes. Complete change from the most disordered structures to the most perfect structures can of course be achieved by changing the structure of the actual polymer chains, and this subject will be considered later in this paper.

Up to the present we have been discussing isotropic structures. In nature and technology, however, a very important part is played by anisotropic polymeric formations — fibres and fibrous materials. Most synthetic fibres are obtained by elongating originally isotropic or almost isotropic fibres. To trace the origin of oriented structures, it is extremely important to know whether relationships exist between the structure, and hence the properties, of oriented fibres and the structure of the original material from which the fibre is prepared by elongation. Orientation, particularly in crystalline polymers, usually takes place abruptly, with the production of so-called "necks". It was observed at an early date[29] that this process occurs as a phase transformation. It might be suggested that the production of a "neck" is accompanied by complete breakdown of the structures which existed in the isotropic polymer and the production of completely new structures in an oriented state. It was recently shown, however, that a direct relationship exists between the original structure and the structure produced on orientation. When a film of crystalline polymer exhibiting a spherulitic structure (for example polypropylene) is extended, the abrupt formation of an oriented polymer is readily observed. If observations are made of individual spherulites, it can be seen that they are preserved in the extended film. They are usually difficult to observe in fibres, since after elongation they become very long and fine, but they can sometimes be readily seen. Fig. 16 shows the conversion of a polypropylene spherulite into the oriented state[30]. It can be clearly seen that the spherulite is preserved after orientation. It can be shown that these elongated spherulites are only pseudomorphs; the interface between the spherulites is preserved, but not their internal structure. If, however, this oriented film is very carefully heated to a temperature several degrees below the melting point of the crystalline polymer, it contracts and returns almost completely to its original dimensions. In the process, the original spherulites are also restored. Thus the elongation of the spherulites, even when it takes place with the formation of a "neck", may be a reversible process. This phenomenon of the reversible deformation of large crystalline formations has been demonstrated for a number of materials and is apparently fairly common[17,31]. From this it follows that the simpler structural elements making up the spherulites or crystals remain unchanged during orientation and that, moreover, they may preserve

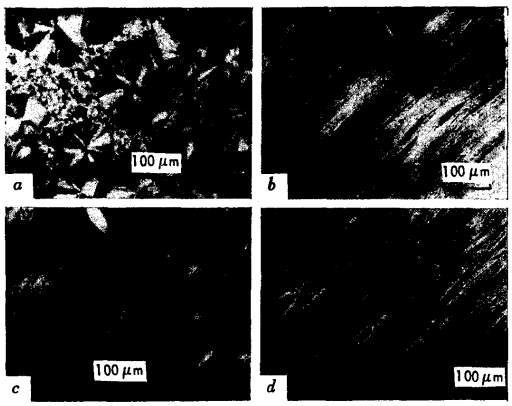

Fig. 16. Change in the structure of polypropylene during extension: *a*) original specimen; *b*)–*d*) extended films.

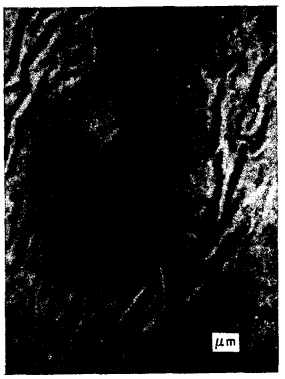

Fig. 17. Conversion of banded structures into crystalline fibrils in polychloroprene.

their mutual arrangement. This phenomenon indicates essentially that large reversible deformations may take place in crystalline polymers without fusion, merely as a result of mutual displacement of the bundles of chains or fibrils.

This phenomenon shows that a close relationship exists between the structures of fibres and the original isotropic materials, and that the structure of fibres begins to be formed even before their orientation. The influence of the structure of fibres on their mechanical properties has been studied for many years, but always on the assumption that the actual orientation process determines the complete structure of the oriented polymer. It is found that the structure of fibres begins to be formed much earlier, even in the isotropic state, and possibly even earlier in melts or solutions, or directly in the polymerisation process! The fact that the structure of oriented fibres influences their properties is generally accepted, and need not be mentioned further.

Thus the development of the properties of solid polymers is closely related to structure formation. This naturally leads to the question of the extent to which the phenomena of structure formation are encountered in elastic polymers and finally the question of where and how the structures begin to be formed — whether they are produced only in the solid state or begin to be produced in the melts or solutions or possibly directly in the processes of polymerisation and polycondensation.

Mention has already been made of the discovery of banded structures in typical rubbers. Similar structures have also been found to be typical of other polymers in the elastic state. The most perfect structural forms in elastomers can be observed only at low temperatures. In crystallising rubbers, however, it is possible to observe the complete change from banded structures to crystalline fibrils and large crystalline formations — spherulites and single crystals. This change has already been described for polybutylene[28]. The conversion of bands into crystalline fibrils is typical, and examples of this change are given in Fig. 17 for polychloroprene. It can be seen that crystallisation is not the original source of order in polymers, but that, on the contrary, ordering in the amorphous state is a necessary prerequisite for crystallisation, which is the last stage in the ordering process. We are thus faced with the question of how the properties of an elastomer change on going from the simplest banded structures to crystalline fibrils and then to spherulites and single crystals.

We are accustomed to the idea that crystallisation always leads to a decrease in elastic properties and to a decrease in elongation. Combined study of properties and structure shows, however, that the earliest stages in crystallisation do not always lead to a decrease in elongation. The production of well-formed fibrils apparently always leads to an increase in strength, and, for a small change in the modulus of elasticity, to an increase in elongation at rupture. We have the effect of "self-reinforcement" which is found in rigid polymers and was first observed clearly for polycarbonates[32,33]. The elastic properties are lost not when the crystalline fibrils are produced but only when the coarsely-crystalline structures — primarily spherulites — are formed. An example of the change from amorphous to crystalline structures is provided by the series of copolymers of ethylene with vinyl acetate. Pure polyethylene has a clearly defined spherulitic structure. The copolymer containing more than 25% of vinyl acetate is a typical amorphous elastomer with a banded structure. With increase in the concentration of vinyl acetate, the crystallinity of the copolymer decreases and the elongation increases, but the strength passes through a maximum. This maximum corresponds to a stage where the crystallinity of the copolymer is still high (Fig. 18). The structures of pure polyethylene and the completely amorphous copolymer, and the structure of the copolymer with maximum elongation, are shown in Fig. 19. The copolymer with maximum elongation shows a clearly defined fibrillar structure and is a transparent typical resilient elastomer.

So far these transitions have been little studied, but even now it can be stated that a definite degree of ordering is necessary for the production of effective mechanical properties in elastomers. The degree of ordering produced in amorphous banded structures is inadequate and a fundamental problem in the production of structures in rubbers is to increase the degree of ordering until well-defined fibrils are formed, both by the use of fillers and by stereospecific polymerisation and copolymerisation. Extremely characteristic phenomena are observed in thin polymer films. Fig. 20 shows the structure of isotactic

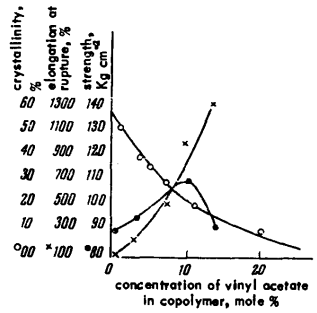

Fig. 18. Composition dependence of the properties of the copolymer of ethylene and vinyl acetate.

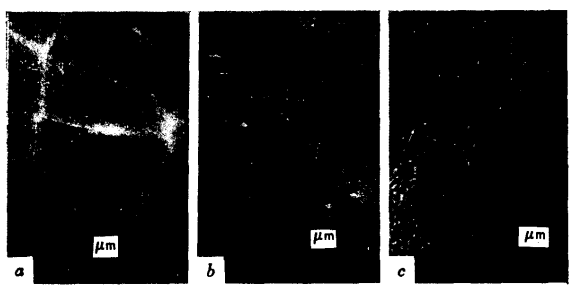

Fig. 19. Structures of pure polyethylene (*a*), the copolymer of ethylene and vinyl acetate at maximum elongation (*b*), and the amorphous copolymer of ethylene and vinly acetate (*c*).

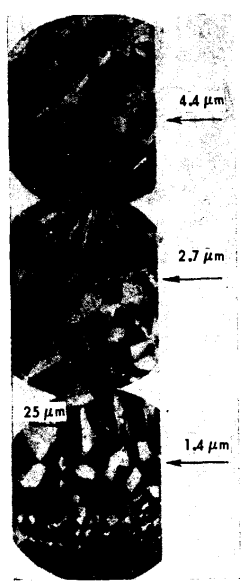

Fig. 20. Change in the structure of isotactic polypropylene with change in film thickness from 1.4 μm to 4.4 μm.

polypropylene in a layer of adhesive whose thickness is varied from several tenths of a micron to one micron. It can be seen that, with decrease in the thickness of the film, the dimensions of the spherulites at first increase, after which, when a definite critical thickness has been reached, they disappear and are replaced by fibrillar structures. Thus for a number of crystalline polymers at least[34], there exists a definite limit of thickness below which large crystalline formations cannot be produced. Thus in the thin polymer layers (produced on surfaces), with thicknesses of several microns, in foams, in reinforced systems, and in systems with high concentrations of fillers, either large or fibrillar structures may be produced depending on the thickness with corresponding consequences for the development of mechanical properties.

Thus detailed study has shown that structure formation is not exceptional but is a common phenomenon for all types of rigid and elastic polymers. It has also been shown that the influence of structures on mechanical properties is important and must always be taken into account.

Where does the formation of structures begin, however? In very dilute solutions polymers are probably present in the form of individual molecules. Similarly it may be confidently assumed that in melts at sufficiently high temperatures all the structures disappear and the polymer is converted into a system of disordered entangled molecules. The change from these infinitely dilute or molten systems to rigid structured polymers, however, may take place over a fairly wide range of temperatures and concentrations. Thus for each polymer it is necessary to estimate the concentrations or temperatures at which structures begin to be produced, since the start of structure formation corresponds to the start of the development of properties.

The fact that very rapid crystallisation takes place in a number of polymers indicates the existence of a fairly high degree of order in the melt. Papers presented at the previous Symposium in Prague gave information on the state of polymers in melts, based on electron diffraction studies[35,37] which showed the existence of a high degree of order in the arrangement of the polymer molecules. The existence of ordered structures in melts is also indicated by the adsorption properties[36] and by the fluidity of the melts[38,39]. Possibly the most graphic demonstration of the existence of structures in the melts is obtained by heating a coarsely-crystalline polymer above its melting point under the microscope and then cooling the melt. In this experiment the microscopic structure of the specimen being studied is very often completely restored. Photographs of polypropylene before and after fusion (with heating to a temperature 20 deg above the melting point) (Fig. 21) are almost indistinguishable. The same spherulites are produced at the same crystallisation centres. This "memory" is preserved in molten polypropylene on heating to a temperature 20–25 deg above its melting point. If the specimen is heated to higher temperatures, however, the number of nuclei gradually begins to decrease and the number of spherulites decreases, with a corresponding increase in their dimensions. Finally, after a definite temperature has been reached (for polypropylene this temperature lies 150–200 deg above the melting point) all traces of the original structures preserved in the melt disappear and the entire crystallisation picture changes sharply. The same polypropylene specimen, after being heated to 350°, has a finer spherulitic structure (Fig. 22). It can be seen how the foundations for the structures are

Fig. 21. Structure of polypropylene film before (*a*) and after (*b*) fusion.

Fig. 22. Structure of polypropylene film after fusion at 350°.

created in the melt and how the temperature conditions in the melt determine the structure and hence the properties of the polypropylene specimen. There is thus no doubt that structures exist in molten polymers although up to the present no one has been able to observe these structures directly.

Quite recently, however, it has been possible to observe directly the formation of structures in solutions. By using as solvents substances which show absolutely no tendency to crystallise and which form glasses on cooling, it is possible to obtain solutions of polymers in the vitreous state. It is highly probable that, when a solution is converted into a glass, it retains the structure which it had in the liquid state. By breaking the glass and taking a replica from the surface of the fracture, it is possible to study the structure of the solutions. The electron-microscope photographs of replicas obtained from 0.1% and 0.5% solutions of poly-α-butylene in vitreous rosin (Fig. 23) show the start of structure formation at a concentration of 0.1% and clearly defined structures at 0.5%.[40]

These results were confirmed by a different method. By dissolving a polymer in a solvent with a low critical point and heating the solution above the critical temperature, we

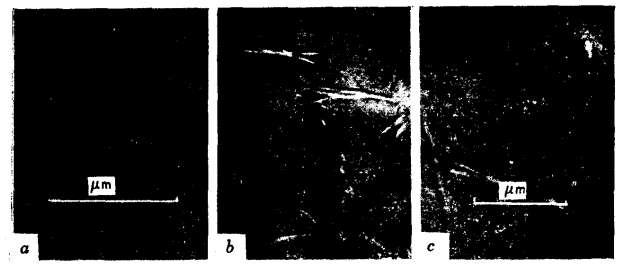

Fig. 23. Replicas from solutions of poly-α-butylene in vitreous rosin at concentrations of 0% (*a*), 0.5% (*b*), and 0.1% (*c*).

obtained a solution in a gas, with the same density as the original liquid. In this case also it may be assumed that the structure of the solution will not change significantly. If we break a heated ampoule containing such a solution in a vacuum, we expand the gas without the production of an interface and scatter the species present in the solution throughout the entire volume of the vessel. If we place at the foot of this vessel pieces of gauze with the thin carrier films usually employed in electron microscopy, we can collect these particles and examine them in the electron microscope. An example is provided by a solution of polybutylene in propane, heated to 115°. This experiment gave results completely analogous to those described above for vitreous solutions[41].

In the same way it is possible to follow the formation of globular structures in solutions. As noted above, almost any polymer can be obtained in the globular state from extremely dilute solutions. With increase in the concentration of solutions containing coiled molecules, however, aggregation of the molecules also begins. In the case of globular formations this leads to an increase in the dimensions of the globules, since the aggregating globules combine together to form larger globules containing not one but an appreciable number of polymer molecules. Rearrangement of the globules into linear structures may take place only at comparatively high concentrations. Fig. 24 shows photographs obtained for solutions of isotactic polyacrylic acid in liquid ammonia with a small quantity of water above the critical temperature. At a concentration of 0.05% each globule contains 1–4 polymer molecules, with increase in the concentration to 0.5% the number of molecules in each globule increases to between 9 and 70, and at a concentration of 1% the number of molecules in each globule increases to 120 and rearrangement to a linear structure begins.

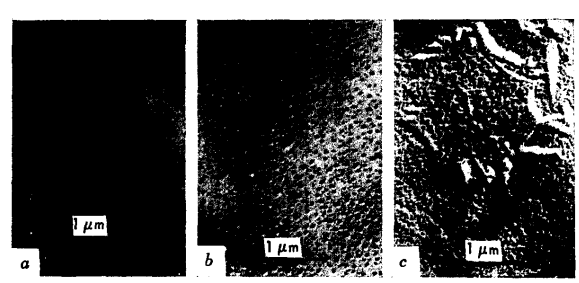

Fig. 24. Structure of isotactic polyacrylic acid in liquid ammonia solution at concentrations of 0.05% (*a*), 0.5% (*b*), and 1% (*c*).

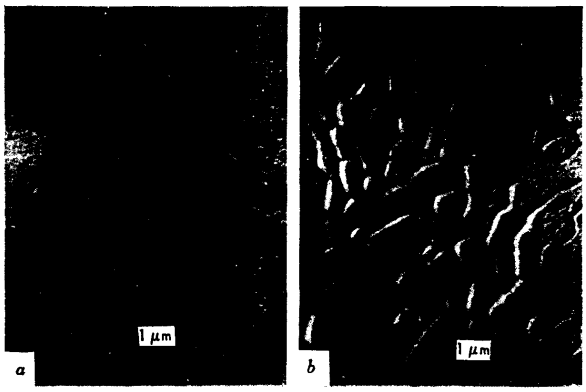

Fig. 25. Structure of polystyrenesulphonic acid in liquid ammonia solution at concentrations of 0.2% (*a*) and 1% (*b*).

Fig. 25 shows analogous photographs for polystyrenesulphonic acid; in 0.2% solution each globule contains between one and twenty molecules, whereas at a concentration of 1% the structure is completely fibrillar.

Thus these few results show that structures are produced in solutions at low concentrations and that concentrated solutions naturally contain structures which are extremely similar to the simplest types of structure found in solid polymers. Nucleation of the structures and hence the start of the development of properties takes place even in comparatively dilute solutions and hot melts.

It is also possible to make the more far-reaching assumption that structures may be produced directly in the polymerisation process. Several years ago the production of coarse fibrous structures was observed on the surface of heterogeneous catalysts during the polymerisation of ethylene and propene[42,43] and the polymerisation of a number of solid monomers[44]. When the temperature of the experiment exceeds the glass temperature of the polymer, however, there is always a danger of molecular rearrangement and the formation of structures as a result of secondary processes. The only polymerisation experiment free from criticism is one in which the monomer and polymer are solid and are at a temperature lower than the glass temperature. Such experiments were carried out recently by polymerising solid monomers directly in the electron microscope, where the electron beam itself initiated the polymerisation. The materials studied were phenylmethacrylamide, *p*-biphenylylmethacrylamide, and sodium acrylate. Fig. 26 shows electron-microscope photographs of polyphenylmethacrylamide and polybiphenylylmethacrylamide obtained by polymerising the solid monomers, and Fig. 27 shows an electron-microscope photograph of sodium polyacrylate obtained under the same conditions.

It can be seen that, instead of the continuous thin film which should have been obtained for regular polymerisation throughout the entire volume of the monomer, typical bundle-like structures are in fact produced, accompanied by a small number of globules. The actual polymerisation process is readily observed under the electron microscope and provides an example of the direct production of structures in the polymerisation process. It is as yet difficult to say anything regarding the extent of such phenomena, but it is now known that they are possible. If, however,

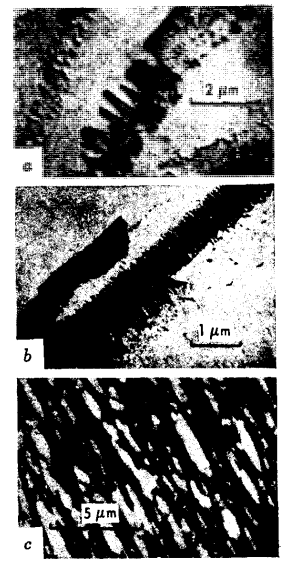

Fig. 26. Structures of polybiphenylylmethacrylamide (*a*) and polyphenylmethacrylamide (*b* and *c*) obtained by polymerisation of the solid monomers.

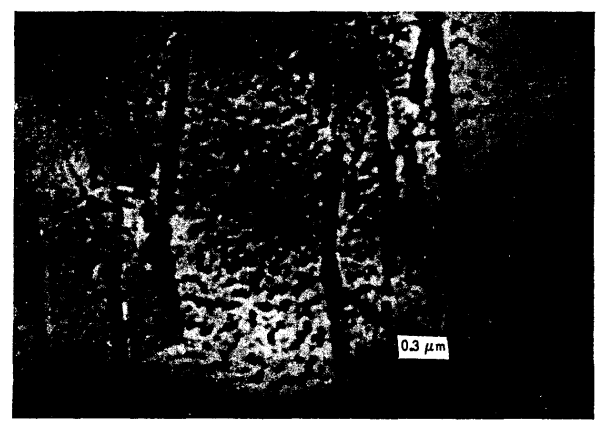

Fig. 27. Structure of sodium polyacrylate obtained by polymerisation of the solid monomer.

structures can be formed directly in the polymerisation process, this can and must influence the polymerisation process itself, particularly the free energy changes during polymerisation. The total free energy change is always equal to the sum of the free energies of conversion of the monomer into the polymeric molecules and the formation of structures from individual polymeric molecules. In most cases, when the heats of polymerisation are large and the polymerisation–depolymerisation equilibria are displaced towards very high temperatures, the free energy changes in structure formation are unimportant. When the heats of polymerisation are small, however, as for example in the polymerisation of rings, structure formation may play an important part and there may even be cases

where polymerisation becomes possible only when structure formation takes place. Several cases are known where polymerisation takes place only when the resulting polymer crystallises and does not take place when the polymer cannot crystallise (α-methylstyrene, α-pyrrolidone, and α-piperidone[45-47]. Crystallisation is most favourable for displacement of polymerisation–degradation equilibria towards polymerisation, but it may be assumed that very strong interaction between the chains and the formation of amorphous structures may be sufficient. Processes such as the polymerisation of nitriles may be possible only as a result of structure formation by the polymeric chains with conjugated double bonds[48].

We cannot deal in detail here with the part played by all structural phenomena in polymerisation and we would merely mention that structure formation also influences the kinetics of polymerisation, leading to the characteristic phenomena of autocatalysis[49], that phase transformations in solid monomers are responsible for very rapid polymerisation in the solid phase[50-54], and that polymerisation in complexes makes it possible to carry out a number of polymerisation processes which are not undergone by the pure monomers[55-59]. An equally important factor is the influence of the state of aggregation of the monomer on the structure of the resulting polymeric molecule. Thus in the polymerisation of diketen, initiated by metallic magnesium, two different isomeric forms of the polymer may be obtained, depending on the state of aggregation of the monomer. Polymerisation of solid monomer obtained by the joint condensation of the vapours of the monomer and metallic magnesium at a temperature several degrees below the melting point gives a polyether. Polymerisation at or above the melting point, however, gives a different isomer — a poly-β-diketone[60]. Similarly, acetaldehyde polymerised in the solid state in the presence of metallic magnesium, introduced into the monomer by joint condensation of the vapours, gives polyacetal. When the same system is polymerised above the melting point, polyvinyl alcohol is formed[61]. In both cases the difference between the polymerisation temperatures above and below the melting point amounts to only a few degrees. The formation of the different polymeric isomers is undoubtedly determined entirely by the state of aggregation of the monomer. Thus it is also necessary to make allowance for the part played by structural phenomena in the polymerisation stage, particularly in the case of polymerisation in the solid state and in those cases where structures are produced directly in the polymerisation process. The most general conclusion to be reached from the foregoing is that structures are extremely common in polymers of all types and that structures are produced at very early stages in the formation of solid polymers in solutions, in melts, and in the polymerisation process. If this is correct, polymers in most cases cannot be regarded as homogeneous systems like ordinary liquids. The occurrence of structure formation implies the existence of interfaces, differences in densities, and irregular distribution of mechanical stresses. This is related to the influence of the structures on mechanical properties. The heterogeneity of polymers should also influence their other properties, and particularly chemical reactions involving the polymers and the processes involved in the swelling and plasticising of polymers.

In fact, low-molecular substances introduced into a polymer may be distributed in different ways. The most usual result is regular distribution of the substance throughout the entire bulk of the polymer, corresponding to true dissolution of the low-molecular substance in the polymer. This leads to corresponding changes in mechanical properties and particularly to a decrease in the glass temperature, proportional to the mole fraction[62] or volume fraction[63] of the added plasticiser.

In polymers showing structure formation, however, another possibility arises. If the low-molecular substance (plasticiser) is insoluble in the polymer but wets it, it may be distributed along the interfaces between the structures, acting as a lubricant between them and thus increasing the mutual mobility of the individual elements of the structure. Very small quantities of plasticiser may then produce very marked effects, but at the same time saturation should take place rapidly and addition of excess plasticiser will not be accompanied by a further decrease in the glass temperature or modulus of the polymer. These phenomena, described as inter-bundle or inter-structural plasticising, have been detected particularly in cellulose esters[64-68]. Fig. 28 shows the dependence of the glass temperature of nitrocellulose on the concentration of various plasticising agents, introduced via the solution. For dibutyl phthalate, which shows unlimited solubility in nitrocellulose, the glass temperature decreases continuously with increase in concentration. Castor oil is insoluble in nitrocellulose, and its addition in very small quantities (see the upper right hand section of Fig. 28) leads to a sharp decrease of the glass temperature, but its effect rapidly reaches a limit beyond which no further change takes place (curve *2* in Fig. 28). We thus see two different types of plasticising — that by a soluble plasticising agent and that by an insoluble plasticising agent, which is distributed only at the interfaces between the structures. The effect of the insoluble plasticising agent is unusually pronounced — the addition of 0.1% produces the same effect as the addition of 10% of the soluble plasticising agent, but saturation takes place equally rapidly. An analogous situation is observed in the plasticising of acetylcellulose. Curve *1* in Fig. 29 illustrates the effect of the soluble plasticising agent 2-methyl-1-nitropropan-2-ol, and curve *3* illustrates the effect of the insoluble plasticising agent butyl stearate, which acts between the bundles. We can see the same typical effect of unusually small quantities of the inter-bundle plasticising agent, with rapid attainment of the limit at a concentration of only 0.05%. The sparingly soluble plasticising agent trimonochloroethyl phosphate occupies an intermediate position.

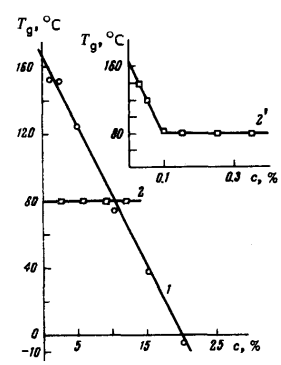

Fig. 28. Dependence of the glass temperature of nitrocellulose on the concentration of plasticiser added via the solution: 1) butyl phthalate; 2) and 2′) castor oil.

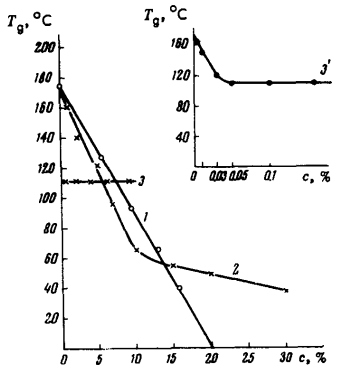

Fig. 29. Dependence of the glass temperature of cellulose triacetate on the concentration of the plasticiser:
1) 2-methyl-1-nitropropan-2-ol; 2) trimonochloroethyl phosphate; 3) and 3′) butyl stearate.

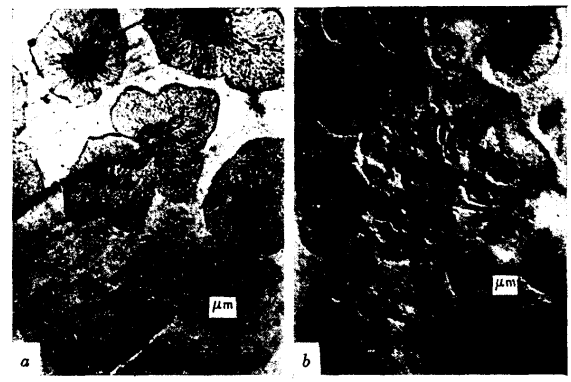

Fig. 30. Successive stages of structure formation in polychloroprene rubber vulcanisates broken down mechanically by rolling (*a* and *b*).

Analogous phenomena have recently been observed for other polymers[69-71].

We must not forget other effects associated with inter-structural plasticising. A small quantity of a low-molecular substance present at the interfaces increases the mobility of the structural formations and facilitates the production of higher supermolecular structures. This is not dangerous in the case of amorphous polymers, but in crystalline polymers it may lead to a sharp increase in the rate of recrystallisation with the formation of brittle structures, so that the result is not plasticising but the production of brittleness[72].

Chemical reactions in polymers also often take place similarly as in heterogeneous systems. A paper presented at the Symposium in Paris described structural phenomena observed in the production of graft polymers. The general conclusion was that the grafting process usually takes place not in the entire bulk of the polymer but only at the interfaces between the structural formations, and that the resulting graft polymers usually show the phenomena of "micro-layer formation", that is a change to heterogeneity[73].

Another example of a chemical process which takes place in polymers similarly as in heterogeneous systems is vulcanisation. It has for long been known that vulcanised rubbers from crystallisable raw rubbers retain the ability to undergo crystallisation. The explanation given was that crystallisation takes place only in small sections of the chains. It has recently been possible to show that rubbers vulcanised in the normal way retain not only their ability to undergo crystallisation but also their abilitiy to form higher structures, as far as the formation of single crystals. Fig. 30 shows the various successive stages of the ordering and crystallisation of polychloroprene, vulcanised by Tonox to a vulcanisation network frequency corresponding to the average production of one bond per 300 carbon atoms. The vulcanised specimens were rolled until the soluble state was attained, after which specimens for electron-microscope study were obtained from solution in carbon tetrachloride. It is obvious that even after vulcanisation the rubber still contained a sufficiently large number of unbranched chains and linear structural formations, without which the formation of large

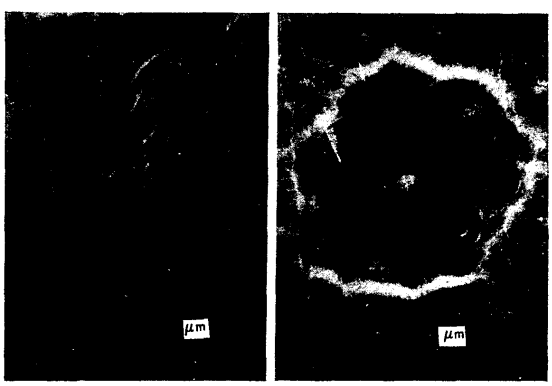

Fig. 31. Structures produced in polychloroprene rubber thermovulcanisates.

structures and single crystals is impossible. This takes place only when the vulcanisation bonds are distributed irregularly in the rubber, which is possible only in heterogeneous systems.

Fig. 31 illustrates analogous structure formation in polychloroprene heat-vulcanisates. Thus thermochemical decomposition also takes place irregularly throughout the entire bulk of the rubber[74,75].

A curious feature is that it is also possible to detect phenomena associated with the presence of structural formations in solutions in the study of chemical reactions involving polymers. In the chlorination of high-density polyethylene in carbon tetrachloride solution in the concentration range 0.1–0.5% at 115–125°, the chlorination product is divided into two fractions immediately after the solution is cooled — fractions soluble and insoluble in cold carbon tetrachloride. The concentrations of chlorine in these fractions differ by a factor of 2–3, the total chlorine concentrations being 14–22% for the soluble fraction and 4–8% for the insoluble fraction. This phenomenon persists up to 130°, after which a homogeneous product is formed, soluble or insoluble in chlorobenzene, depending on its chlorine content. A curious feature is that this

temperature is extremely close to the melting point of polyethylene crystals and evidently corresponds to complete breakdown of the structural formations in solution. The experiments were carried out by rapidly mixing solutions of polyethylene and a solution of chlorine in chlorobenzene, to avoid possible non-uniformity in the chlorination by the gas[76]. Analogous phenomena are observed in the chlorination of gutta-percha[18].

In this paper an attempt has been made to present basic data on the formation of structures in polymeric substances in all their states, on their nucleation, and on the part which they play in polymerisation processes, the development of mechanical properties, and their influence on the chemical behaviour of polymers. Structural phenomena must not now be regarded as exceptional but as an integral part of all processes leading to the development of the most important properties of polymers.

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CHARACTERISTIC FEATURES OF NON-EQUILIBRIUM POLYCONDENSATION†

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† Reported at the International Symposium on Macromolecular Chemistry in Prague, 1965.

I. INTRODUCTION

Recently there has been extensive development of new polycondensation processes leading to the preparation of a number of hetero-chain polymers which include many compounds of great practical interest since these are substances with high thermal stability, interesting electrophysical properties, biological activity, etc. Among these processes mention must be made in particular of interfacial polycondensation, dehydropolycondensation, and especially oxidative dehydropolycondensation, and also the polyrecombination reaction, the polycyclisation reaction, and certain others.

For clarity we shall adopt the conventional definition of polycondensation as a process involving the formation of high-molecular-weight compounds in which in addition to the polymer a low-molecular-weight product is formed, most often water, hydrogen chloride, and similar substances. Because of this the elementary composition of the polymer formed differs from that of the initial monomer or the initial mixture of monomers.

In the general case the polycondensation reaction of two starting materials can be represented by the following equation:

$$x\text{a}-\text{A}-\text{a}+x\text{b}-\text{B}-\text{b}\rightarrow\text{a}-(-\text{AB}-)_x-\text{b}+2(x-1)\text{ab}$$

and in the case where both functional groups enter into the composition of the same initial molecule, the reaction equation is

$$x\text{a}-\text{A}-\text{b}\rightarrow\text{a}-(-\text{A}-)_x-\text{b}+(x-1)\text{ab}.$$

II. TYPES OF POLYCONDENSATION

We now know that, depending on the structure of the starting materials and the method of carrying out the reactions, polycondensation can be achieved in two different ways, namely: (1) as equilibrium polycondensation and (2) as non-equilibrium polycondensation. In addition there are probably certain reactions which exhibit the features of both types of polycondensation. Unfortunately reactions of this intermediate type have so far been little investigated.

A characteristic feature of equilibrium polycondensation is a low equilibrium constant. Very many examples of equilibrium polycondensation are known. Examples which have been particularly thoroughly investigated are the formation of polyamides or polyesters in the reactions, on heating, between dicarboxylic acids and diamines or glycols.

Equilibrium polycondensation constitutes a classical method of synthesising polymers which has been known for a long time. It has been studied thoroughly in many instances and its principal features have been established in a large number of investigations and have been described in reviews and monographs[1-9].

On the other hand, non-equilibrium polycondensation is a new process which was discovered relatively recently

and therefore it has so far been little investigated and its principal features are still the subject of study.

The present review represents a first attempt to examine the results obtained in the study of non-equilibrium processes and to elucidate the specific features of such reactions.

1. Non-Equilibrium Polycondensation

At the present time there are comparatively few cases of non-equilibrium polycondensation which have been investigated in detail. However, it is now possible to divide such reactions into two groups. The first group includes reactions which occur at a high rate under mild conditions, at low temperatures, where exchange interactions cannot occur. An example is the formation of polyamides or polyesters from the chlorides of dicarboxylic acids and diamines or dihydric phenols, which takes place very rapidly under conditions of interfacial polycondensation or in solutions.

The second group of non-equilibrium reactions includes cases of polycondensation which, although taking place fairly slowly at high temperatures, can nevertheless be classified as non-equilibrium polycondensation reactions because the polymers formed are very stable under the reaction conditions and are incapable of hydrolysis and other degradative conversions, such as, for example, interaction with the starting materials or the growing macromolecules. As a result of this stability of the macromolecules formed, degradative and other exchange processes are absent during the reaction, and this results in the irreversibility and the non-equilibrium nature of the process as a whole. Examples of such reactions are the formation of various polymers in dehydropolycondensation, polyrecombination, polycyclisation, and certain other processes, which will be examined below.

The chemical characteristics of the non-equilibrium polycondensation reactions enumerated above will be considered first.

2. Interfacial Polycondensation

Interfacial polycondensation, which was developed by Morgan[10], is carried out by mixing the reactants dissolved in two immiscible solvents, for example in water and in a hydrocarbon, hence its name: polycondensation at the interface between phases‡.

Interfacial polycondensation opens up new possibilities for the synthesis of many polymers, polyamides, polyesters, and many others and for this reason has greatly attracted the attention of investigators. In the synthesis of polyamides the reaction between the initial acid dichloride and the diamine proceeds according to the equation

$$x\mathrm{ClCOR'COCl} + x\mathrm{H_2NRNH_2} \rightarrow [\mathrm{—COR'CONHRNH—}]_x + 2x\mathrm{HCl}.$$

Interfacial polycondensation is based on the acylation of diamines or bisphenols with acyl or aryl chlorides in the presence of aqueous alkali. The principal feature of this reaction is the use of reactive starting materials such as the chlorides of dicarboxylic acids, which ensures a high reaction rate.

Interfacial polycondensation was studied in detail and reviewed by Frunze et al.[11]. Polymers are synthesised in this way in practice. Polycarbonates, polyamides, polyurethanes, polyarylates, and certain other high-molecular-weight compounds are obtained in this way.

When gaseous acid chlorides are used, there arises a new modification of this process, "gaseous polycondensation", which, as shown by Sokolov et al.[12], exhibits somewhat different features.

3. Polycondensation in Solution

A second variety of polycondensation processes which take place when the chlorides of dicarboxylic acid are used is polycondensation in solution which may be carried out both at low and elevated temperatures. The polycondensation of bisphenols with the chlorides of dicarboxylic acids in solution (with heating) was used successfully by Korshak and Vinogradova[13] for the synthesis of polyarylates (polyphenylene esters of aromatic dicarboxylic acids). High-boiling solvents are used (Dinile, ditolymethane, Sovol, α-chloronaphthalene, and others), which made it possible to lower the viscosity of the reaction mass and to obtain high-molecular-weight polyesters[14]. Kwolek and Morgan[15] showed that in low-temperature polycondensation in solution in chloroform and other organic solvents it is possible to obtain polyamides, polysulphonamides, polyesters, and polyurethanes, tertiary amines being sometimes used. In solution in dimethylacetamide, hexamethylphosphoramide, hexamethylphosphoramide etc. polypyromellitimides, polyoxadiazoles, and other polymers are obtained[41,43].

4. Dehydration Polycondensation

Homofunctional dehydration polycondensation of silanediols and silanetriols, leading to the formation of organosilicon polymers[16], is also a non-equilibrium reaction, which can be represented by the equation

$$\gtrless\mathrm{Si—OH} + \mathrm{HOSi}\lessgtr \longrightarrow \gtrless\mathrm{Si—O—Si}\lessgtr + \mathrm{H_2O}.$$

It goes to completion even in the presence of an excess of water, since the reverse reaction, involving the hydrolysis of siloxane bonds, does not take place at low temperatures[17]. Since this reaction is the main stage in the synthesis of polyorganosiloxanes by hydrolytic polycondensation, the entire process may be regarded as a non-equilibrium one. This is particularly so because in most cases the first stage is the non-equilibrium hydrolysis of the chlorine atom or other groups linked with the silicon atom.

The formation of polyethers or glycols, according to the equation

$$x\mathrm{HO—R—OH} \rightarrow (\mathrm{—OR—})_x + x\mathrm{H_2O},$$

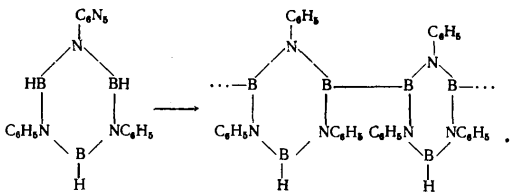
is also a case of non-equilibrium polycondensation.

5. Dehydropolycondensation

Yet another example of non-equilibrium polycondensation is dehydropolycondensation which has been used for the synthesis of high polymers only recently. Korshak

‡ The Russian author calls this type of polycondensation interphase polycondensation and refers to interfacial polycondensation as a second name for this process (Ed. of Translation).

et al.[18] showed that it may involve simple removal of hydrogen, as, for example, in the synthesis of organoboron polymers by heating *N*-triphenylborazole:



The most interesting example of reactions of this type is oxidative dehydropolycondensation which is based on the oxidation of hydrocarbons or their derivatives by oxygen or other oxidising agents and takes place with removal of hydrogen by the oxidising agent.

By oxidative dehydropolycondensation of acetylene in the presence of copper salts,

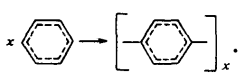
$$x\mathrm{HC{\equiv}CH} \longrightarrow [-\mathrm{C{\equiv}C}-]_x + x\mathrm{H_2O},$$

the present author obtained a new carbon polymer — "carbene".[9] The application of this reaction to diacetylene compounds of the type HC≡C–R–C≡CH enabled several investigators[20–23] to obtain a large number of linear polymers of a new type having the general formula

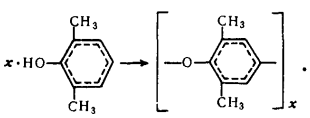
$$[-\mathrm{C{\equiv}C{-}R{-}C{\equiv}C}-]_x,$$

containing triple bonds in the chain together with phenyl and other groups.

Another example is the synthesis of polyphenylene by the oxidation of benzene in the presence of aluminium chloride and cuprous chloride, discovered by Kovacic and Kyriakis[24], which takes place as follows:



Fox and coworkers[25] showed that the oxidation of 2,6-dimethylphenol by atmospheric oxygen in the presence of a pyridine-copper complex involves a reaction leading to the formation of polyphenylene ethers:

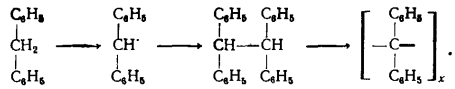


The polyethers obtained in this way are chemically stable and are of practical interest.

6. Polyrecombination

Another new example of non-equilibrium polycondensation reactions is polyrecombination. Recently increasing attention has been paid to the problem of synthesising polymers from substances which are not monomers in the strict sense of this term, i.e. they do not contain double bonds, rings, or other functional groups capable of entering into polymerisation or polycondensation reactions. One of the possible approaches to the solution of this problem involves the use of the polyrecombination reaction, discovered by Korshak et al.[26], as a result of which polymers can be obtained from a wide variety of classes of organic substances, such as saturated hydrocarbons, ethers, ketones, amines, phenols, nitriles, aldehydes, alcohols, "organoelemental" compounds, and many other substances incapable of being polymerised in the usual way[20,26–29].

Polyrecombination is a method of synthesising polymers, which in the case of diphenylmethane can be represented by the equation



The fundamental processes in polyrecombination are the formation and recombination of free radicals produced in the decomposition of t-butyl, benzoyl, and other acyl peroxides. A characteristic feature of the monomers used in polyrecombination is the presence of a labile hydrogen atom which can be readily removed by free radicals. If the monomers have two reactive hydrogen atoms, soluble products are obtained, and when there are three and more such atoms the products are insoluble three-dimensional polymers[27].

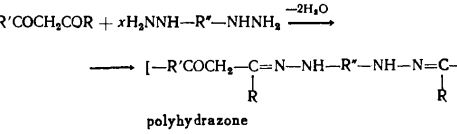
7. Polycyclisation

Polycyclisation is an extremely interesting new example of non-equilibrium polycondensation. It is a new type of reaction leading to the formation of polymers with a ring-chain structure which are interesting because they include a number of substances with exceptionally high thermal stability. Unfortunately at present there are as yet few data concerning the mechanism of the polycyclisation reaction, but those that are available suggest certain generalisations and make it possible to put forward a mechanism in a general, schematic form for these reactions, which appear to be two-stage processes.

The first stage is often an equilibrium reaction of the usual type, which takes place on heating of the reaction mixture and leads to the formation of polyamides, polyesters, polyhydrazones, and similar compounds, depending on the structure of the starting material. The features of this stage do not differ in general from those known for similar reactions. However, in many cases the first stage of this process can also be carried out in a non-equilibrium manner by interfacial polycondensation or reaction in solution.

The second stage involves the cyclisation itself, i.e. the closure of the heterocycle which is characteristic of this reaction. In most cases this stage constitutes true non-equilibrium polycondensation because it involves irreversible formation of stable aromatic rings.

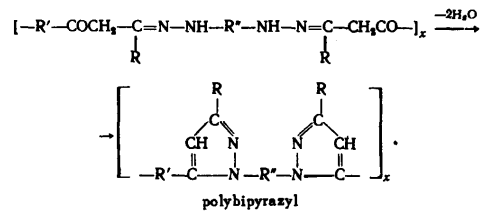
Thus in synthesis of polypyrazoles, obtained for the first time by Korshak et al.[30,31], the intermediate is a polyhydrazone formed in the reaction between bisdiketones and dihydrazines or dihydrazides which can be represented as follows:



polyhydrazone

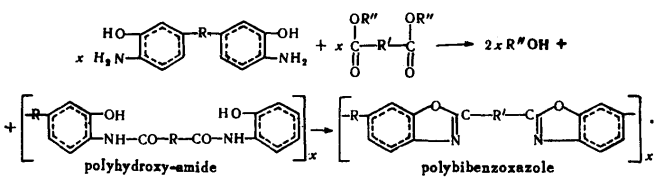
This stage is probably reversible, since condensation of dicarbonyl compounds with dihydrazines is known to be an

equilibrium process[32]. In the second stage the polyhydrazone is converted into a polypyrazole by the following reaction:



polybipyrazyl

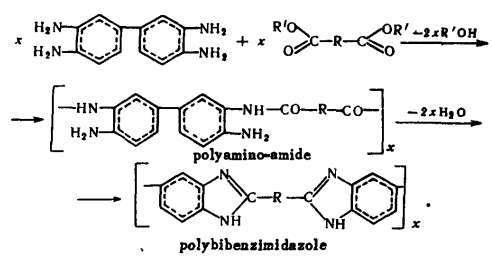
The same picture was established also in the synthesis of polybenzoxazoles obtained by a number of investigators[33-36,58]. The reaction involves the intermediate formation of polyhydroxy-amides formed from dihydroxy--diamines and dicarboxylic acid esters:



polyhydroxy-amide polybibenzoxazole

The polyhydroxy-amide formed in the first stage is unconverted by cyclisation into polybibenzoxazole. Both in this and the preceding case the reaction can be carried out with isolation of the intermediate product or can be taken at once to completion with preparation of the ring-chain polymer.

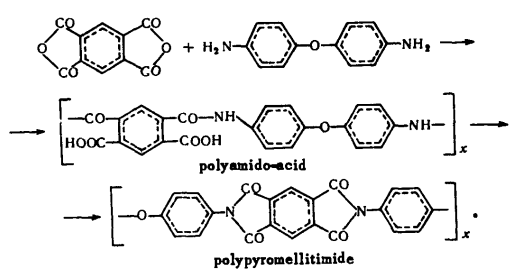
The formation of polybenzimidazoles, which has been investigated in detail by Marvel[37] and other investigators[36,38-40], probably involves the intermediate formation of a polyamino-amide:



polyamino-amide

polybibenzimidazole

The formation of polypyromellitimides takes place in the same way[41]:



polyamido-acid

polypyromellitimide

The polycyclisation process has undergone extensive development as a result of the work of Marvel[37] and other investigators and has led to the preparation of a large number of polymers incorporating in the chain heterocycles such as triazole[42], imidazole[36,37-40], pyrazole[30,31], oxadiazole[43-45], oxazole[33-36], triazine[46], thiazole[45], pyromellitimide[41], quinoxaline[47], and others.

Having examined the most important examples of non--equilibrium polycondensation, we shall now consider certain data concerning reactions of this type. The most important characteristics of equilibrium and non-equilibrium polycondensation are the presence of exchange reactions in the first case and their absence in the second, the effect of the excess of the reactants, and finally the fractional composition of the polymers formed. The available literature data on these problems will be examined below in the sequence indicated.

III. EXCHANGE REACTIONS

The significant difference between equilibrium and non--equilibrium polycondensation consists in the fact that in the first case exchange reactions take place between the growing polymer macromolecules and also between the latter and the starting materials or low-molecular-weight reaction products (water and others). For this reason, the macromolecules formed in the equilibrium process change during its course, which is reflected in the first place in the fractional composition (polydispersity) of the polymer, while in a non-equilibrium reaction exchange processes do not occur and therefore the distribution of the polymers formed with respect to molecular weight is different.

At temperatures normally used for equilibrium polycondensation, exchange reactions between individual macromolecules play a considerable role. This has been demonstrated in a number of cases. Thus on heating of two specimens of different polyamides there is a gradual change in melting point; for example, Fig. 1 shows the change in melting point when a mixture of polyhexamethyleneadipamide and polyhexamethyleneisophthalamide is heated[48].

The melting point of the mixture falls until the melting point of the corresponding copolymer, a mixed polyamide is reached. The mixture of the two homopolymers is converted into the copolymer via a block-copolymer stage which exists for a limited period. Fig. 2 shows the variation of the content of these three products in the reaction medium in the course of the process[49].

These reactions also take place when mixtures of polymers as different as polyamides and polyesters are heated.

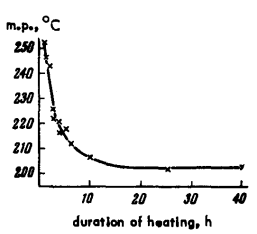


Fig. 1. Variation of the melting point of a mixture of polyhexamethyleneadipamide and polyhexamethyleneisophthalamide as a function of the duration of heating.

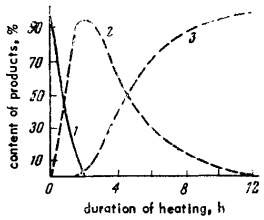


Fig.2. Variation of the content of the homopolymer (curve 1), block-copolymer (curve 2), and mixed polyamide (curve 3) with the duration of heating of a mixture of homopolyamides.

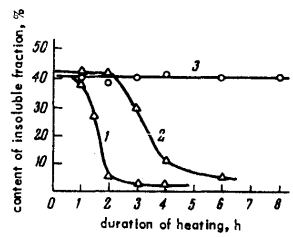


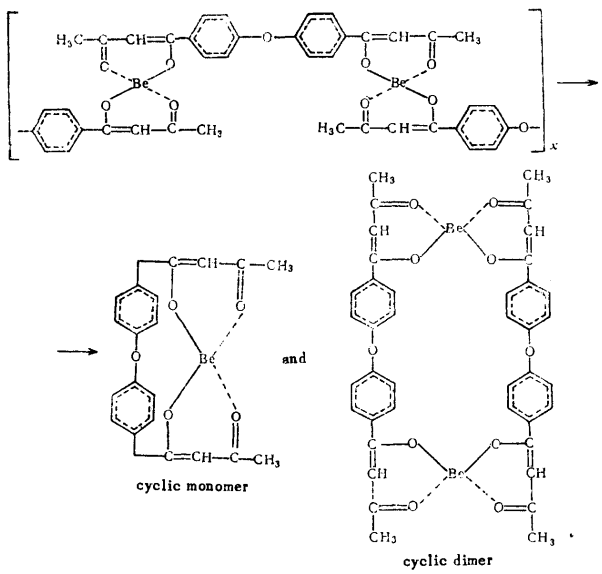
Fig.3. Variation of the content of the benzene--insoluble fraction with the duration of heating of a mixture of polyhexamethylenesebacamide and polyhexamethylenesebacate at various temperatures: 1) 290°; 2) 280°; 3) 260°.

At a temperature in excess of 280°, and in the presence of catalysts even at 260°, a mixture of polyamide and polyester is converted into the copolymer, polyamido-ester, the process being accompanied by a change in melting point and solubility of the mixture of the starting polymers[50].

Fig.3 shows the variation of the content of the benzene--insoluble fraction when a mixture of polyhexamethylenesebacamide and polyhexamethylenesebacate is heated at various temperatures. It is seen that at 280° and above vigorous exchange reactions take place and result in the formation of benzene-soluble polyamido-ester and the disappearance of the insoluble polyhexamethylenesebacamide.

Exchange reactions take place particularly readily in coordination polymers of the chelate type. When a mixture of two coordination polymers of different molecular weights is heated, exchange takes place and results in the molecular weight being averaged out[51]. These polymers have been found to undergo an unusual exchange reaction — exchange of one metal for another. Thus when copper acetylacetonate acts upon the chelate polymer of beryllium, the latter metal is displaced and a chelate polymer of copper is formed[49]. Exchange reactions can occur very readily in chelate polymers, particularly in dilute solutions.

Korshak et al.[51,52] found that only brief heating of a dilute solution of the polymer is sufficient for complete degradation, resulting in the conversion of the polymer into cyclo-oligomers:



When these cyclic oligomers are heated in more concentrated solutions, they are reconverted into the initial polymer. Thus here we encounter for the first time an example of a reaction involving total reversibility of the ring–polymer conversion, the equilibrium position of which depends on the concentration of the solution. The examples of exchange reactions quoted for various polymers clearly demonstrate this feature of the equilibrium polycondensation process.

On the other hand, the products formed in a non-equilibrium polycondensation reaction, under conditions ensuring their formation, are quite incapable of undergoing exchange processes. This applies both to synthesis of polymers under the mild conditions of interfacial polycondensation and to the synthesis of polymers at high temperatures under severe conditions in the case of the polycyclisation and polyrecombination reactions.

Thus on heating a mixture of products obtained by polycyclisation, exchange reactions do not occur. Korshak et al.[42] showed that, after heating for 20 h at 270° a mixture of two poly-4-amino-1,2,4-triazoles, obtained by the polycondensation of hydrazine with adipic acid in one case and with sebacic acid in the other, it is possible to isolate unchanged the initial polymers, which indicates the absence of exchange reactions between their macromolecules. Mixed poly-4-amino-1,2,4-triazoles could be obtained only by the polycondensation of the initial monomer, i.e. hydrazine, with a mixture of the two dicarboxylic acids[42].

IV. THE RULE OF THE NON-EQUIVALENCE OF FUNCTIONAL GROUPS

The molecular weight of polymers obtained by polycondensation is determined in the first place by the relative proportions of the starting materials when the reaction takes place between two different components. In this case the *"rule of the non-equivalence of functional groups"* operates, according to which the excess of one of the starting materials, provided that it is not removed

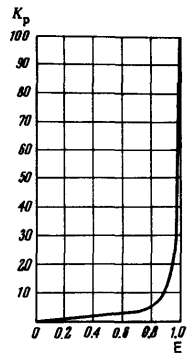


Fig. 4. Variation of the polymerisation coefficient (K_p) with the equivalence coefficient (E).

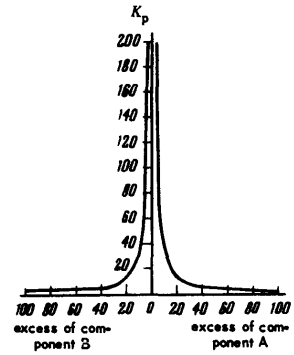


Fig. 5. Variation of the limiting value of the polymerisation coefficient (K_p) with the excess of one of the starting materials (mole %).

during the reaction, lowers the molecular weight to an extent proportional to the degree of this excess.

If the reaction is represented in the general form

$$xa - A - a + (x+1)b - B - b \rightarrow b - B - [-A - B -]_x b + 2xab$$

the equivalence coefficient, characterising this relation, can be expressed as follows[53]:

$$E = \frac{x}{x+1}$$

Fig. 4 shows graphically the relation between the equivalence coefficient and the polymerisation coefficient for the polymer being formed. It is readily seen that the closer are the relative amounts of the starting materials to equivalent proportions the higher is the polymerisation coefficient of the polymer.

The existence of a definite relation between the excess of one of the starting materials and the size of the molecule of the polymer formed leads to the following expression[54]:

$$K_p = \frac{100}{q},$$

where K_p is the polymerisation coefficient and q the excess of one of the substances expressed in mole per cent. We may note that this excess plays an additional role in equilibrium polycondensation. It causes the degradation of the growing chains and influences the polydispersity of the polymer, decreasing it.

This relation between the polymerisation coefficient and the amount of the excess component is represented graphically by two branches of a hyperbola (Fig. 5).

The validity of this relation for all the cases of equilibrium polycondensation investigated has been demonstrated for a large number of examples[55]. This relation holds also in non-equilibrium polycondensation, as can be seen from Fig. 6, where the results obtained in the synthesis of poly-2,2′-(octamethylene)-5,5′-dibenzimidazole in the presence of an excess of one of the initial substances[40], are plotted. Here the presence of an excess of each of the starting materials, i.e. both tetramine and the dicarboxylic acid ester, also results in a lowering of the molecular weight of the polymer obtained.

In practice a cessation of the growth of the molecular weight is observed at comparatively early polycondensation

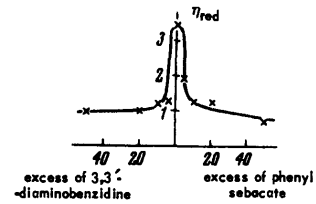


Fig. 6. Variation of the reduced viscosity of a solution of polybenzimidazole with the ratio of the starting materials (mole %).

stages, which leads to a departure of the curve from the theoretical form shown in Fig. 5. This can be explained by the presence of a number of side-reactions and also by the fact that usually all the functional groups are not completely utilised in polycondensation. For this reason, the relation between the molecular weight and the excess of the starting materials observed in practice has the form shown in Fig. 7.[55]

The presence in the reaction mass of monofunctional compounds of a similar chemical type exhibits the same effect as the excess of the starting materials. This behaviour was observed earlier for a large number of examples of equilibrium polycondensation reactions and has been found also in non-equilibrium polycondensation. Fig. 8

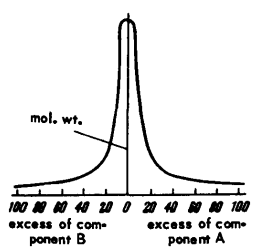


Fig. 7. A schematic representation of the experimentally observed relation between the molecular weight and the excess of the starting material (mole %).

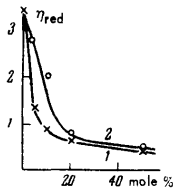


Fig. 8. Variation of the reduced viscosity of polybenzimidazole with the amount of added monofunctional reagent:
1) stearic acid; 2) α-naphthylamine.

shows the effect of added monocarboxylic acid or monoamine on the molecular weight of the polybenzimidazole formed[40].

A similar relation holds also in other cases. For example, in interfacial polycondensation of hexamethylenediamine with the chloride of adipic acid the molecular weight of the polyamide formed decreases in proportion to the amount of added butyryl chloride[11] (Fig. 9).

The same effect is observed when butylamine is introduced into this reaction, as shown in Fig. 10.

In the polycondensation of dian§ with the chloride of isophthalic acid the addition of benzoyl chloride or phenol also causes a corresponding decrease of the molecular weight[11]. This is shown in Figs. 11 and 12.

The present author observed a relation between the molecular weight of the polymer formed and the amount of peroxide used in a polyrecombination reaction[27]. Fig. 13

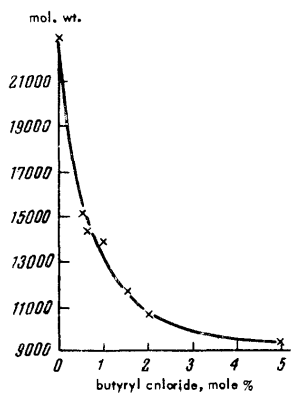


Fig. 9. Variation of the molecular weight of polyamide with the amount of added butyryl chloride.

§ Bis-(p-hydroxyphenyl)dimethylmethane (Ed. of Translation).

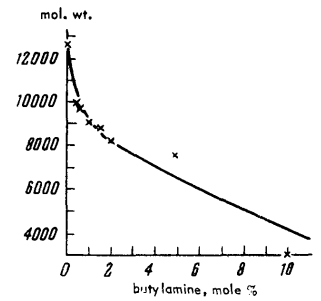


Fig. 10. Variation of the molecular weight of polyamide with the amount of added n-butylamine.

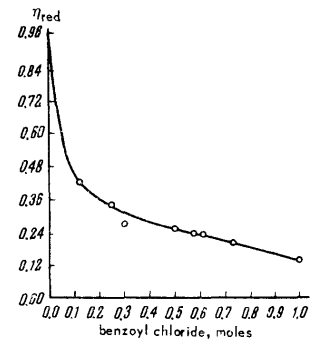


Fig. 11. Variation of the reduced viscosity of polyarylate with the amount of added benzoyl chloride.

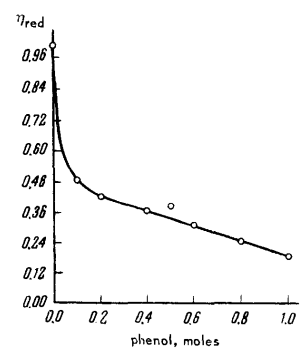


Fig. 12. Variation of the reduced viscosity of polyarylate with the amount of added phenol.

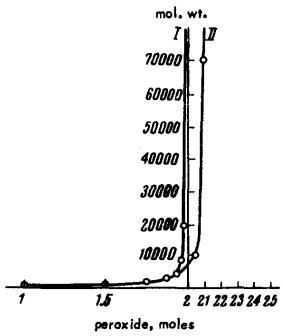


Fig. 13. Variation of the molecular weight of polydiphenylmethylene with the peroxide : : hydrocarbon ratio.

shows the calculated and observed relations between the molecular weight of polydiphenylmethylene and the amount of peroxide used for the polyrecombination. It is seen that the maximum molecular weight is attained when about two moles of peroxide are consumed per mole of the initial hydrocarbon.

V. MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS

Polymers synthesised by non-equilibrium polycondensation exhibit a wider molecular weight distribution than polymers obtained by equilibrium methods. Thus in the case of polyarylates prepared by interfacial polycondensation or reactions in solution at an elevated temperature it was found that the former show a wider distribution than the latter. To account for this difference, it may be pointed out that the polydispersity coefficient M_w/M_n for the former is about 1.5 and for the latter about 2.0. The Table presents data obtained in a study of the molecular weight distribution of polyarylate specimens prepared by the polycondensation of isophthalic acid chloride with two bisphenols under different conditions[56].

We may point out here that polycondensation at an elevated temperature is probably of an intermediate type, since in this case there is no reverse degradative reaction between the polymer and hydrogen chloride but there is a degradative reaction between the polymer formed and the initial bisphenol. Polyesters formed in equilibrium polycondensation show a smaller polydispersity.

The Table shows that the molecular weight distribution of the polyarylates prepared by interfacial polycondensation approaches that predicted by the theory put forward by Flory[1]. Polyamides were found to show a considerable difference in the polydispersity of the products obtained by interfacial condensation and at high temperatures.

Fig. 14 shows curves characterising the fractional composition of polyhexamethylenesebacamide obtained by the interfacial process and poly-ϵ-caproamide obtained in the melt[57]. The much wider molecular weight distribution of the interfacial polycondensation products is clearly evident.

Study of the polymers prepared by polyrecombination showed that they are distinguished by an even greater degree of polydispersity.

TABLE. The polydispersity coefficients of the polyarylates obtained by various methods from isophthalic acid and diols.

Polyarylate based on	Polycondensation in solution		Interfacial polycondensation	
	M_w/M_n from fractionation	degree of completion of reaction	M_w/M_n from fractionation	degree of completion of reaction
bis-(4-Hydroxyphenyl)methane	1.52	0.9795	2.03	0.9934
2,2-bis-(4-Hydroxyphenyl)-propane	1.68	0.9845	2.06	0.9810
ditto	1.60	0.9818	2.03	0.9855

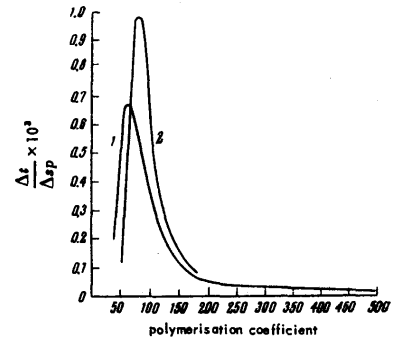


Fig. 14. Fractional composition of polyhexamethylenesebacamide (curve 1), obtained by interfacial polycondensation, and poly-ϵ-caproamide (curve 2).

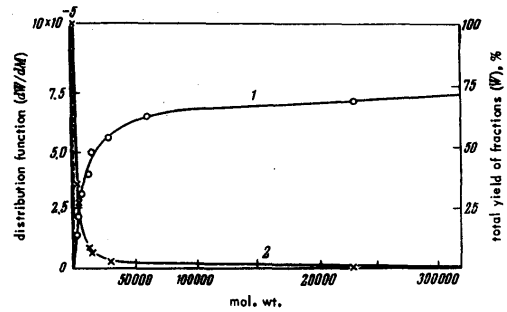


Fig. 15. Molecular weight distribution of polydiphenylmethylene: 1) integral curve; 2) differential curve.

Fig. 15 shows that the molecular weight distribution of polydiphenylmethylene is very wide[29]. The polydispersity coefficient calculated for this polymer proved to be 43. Hence it resembles in this respect high-pressure polyethylene which exhibits a very wide molecular weight distribution.

In conclusion, we may note that examination of the available data makes it possible to elucidate a number of specific features distinguishing non-equilibrium polycondensation. On the basis of the results discussed, we may

conclude that a new field of polycondensation reactions, non-equilibrium polycondensation, has arisen, whose further development and study will permit an even more extensive application of this new method of synthesis of polymers.

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ALKYLATION OF CYCLOALKANES, OXACYCLOALKANES, AND ARALKANES

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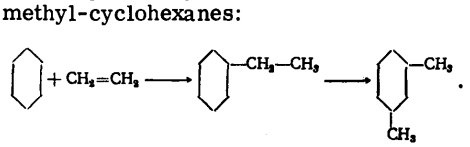
1. INTRODUCTION

Advances in the chemistry of fuel are closely connected with the development of studies in the field of alkylation. Beginning with the middle of the nineteenth century, work on the alkylation of aromatic hydrocarbons became widely known. The search for new methods of synthesis of high-octane components led to the discovery of alkane alkylation reactions. The extensive experimental data in this field have been described systematically in a number of reviews.

Comparatively recently new fields of application of the alkylation reaction have been discovered. This reaction has been extended to the alkylation of cycloalkanes, cyclic ethers (oxacycloalkanes), and the side-chain of aliphatic-aromatic hydrocarbons (aralkanes).

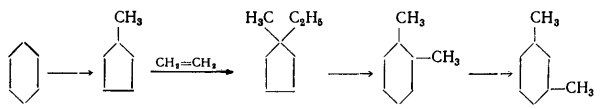
2. ALKYLATION OF CYCLOALKANES IN THE PRESENCE OF ACID CATALYSTS

In the presence of acid catalysts the composition of the alkylation products depends on the structure of the cycloalkane and the nature of the catalyst. When cyclohexane is alkylated with ethylene in the presence of aluminium chloride at 50–75°, a mixture containing 1,3-dimethylcyclohexane, tetramethylcyclohexane, and hexaethylbenzene was obtained[1] instead of the expected ethylcyclohexane. In Ipatieff's view, the absence of the direct alkylation products, ethylcyclohexane and diethylcyclohexane, can be explained by their isomerisation to dimethyl- and tetramethyl-cyclohexanes:



This hypothesis is consistent with the data of Grignard[2], who showed that in the presence of aluminium chloride, ethylcyclohexane indeed isomerises to dimethylcyclohexane. The presence of hexaethylbenzene in the catalytic reaction mixture proves the intermediate formation of hexaethylcyclohexane, which is then dehydrogenated under the reaction conditions[3].

Schmerling[4] holds a different view. He believes that the alkylation process is preceded by the isomerisation of cyclohexane to methylcyclopentane after which the alkene adds to the tertiary carbon atom:



This mechanism is supported by the fact that, in the presence of boron trifluoride, cyclohexane does not react with ethylene, since, unlike aluminium chloride, boron trifluoride does not cause the isomerisation of cyclohexane to methylcyclopentane under the alkylation conditions. The formation of hexaethylbenzene is explained by the dehydrogenation of cyclohexane and subsequent alkylation of benzene.

In the alkylation of cyclohexane with propene[5] in the presence of aluminium chloride at 10–45° polymethylated cyclohexane, dicyclohexyl, alkylated dicyclohexyl, and 2,6-dimethyldecalin are formed in the catalytic reaction mixture[6]. The propylcyclohexane formed in the alkylation of cyclohexane isomerises to polymethylated cyclohexane. The alkylation of cyclohexane with isobutene proceeds with more difficulty, since under the reaction conditions the latter tends to polymerise[5]. In the reaction between cyclohexane and di-isobutene in the presence of aluminium chloride, alkylated cyclohexanes boiling in the range 170–250° were obtained[7].

After passing a mixture of cyclohexane and ethylene over Ni/Al_2O_3 at 300°, 5% of toluene was isolated from the reaction mixture[8]. According to Komarewsky, cyclic hydrocarbons are not alkylated under the conditions described. The formation of toluene is explained by the dehydrogenation of cyclohexane to benzene[9], the alkylation of the latter with ethylene to ethylbenzene, and the decomposition of ethylbenzene with formation of toluene and methane[10].

When an equimolar mixture of cyclohexane and ethylene is passed over Cr_2O_3/Al_2O_3 at 475°, ethylbenzene is formed[11].

In the presence of sulphuric acid, neither cyclopentane nor cyclohexane react with alkenes[12,13].

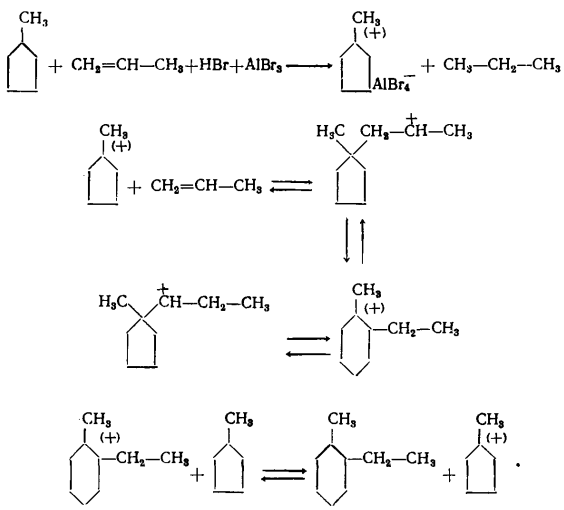
A number of patents[14-16] describe the alkylation of cycloalkanes with alkenes in the presence of mercaptans and a small amount of oxygen. The process is carried out at 300–450° and a pressure of 150–175 atm. The effects of pressure, component ratio, and various promoting agents have been investigated. Under optimum conditions the degree of reaction of the alkenes reaches 79%.

It is also recommended that cycloalkanes be alkylated in the presence of phosphoric acid on carriers[17] and catalysts based on hydrofluoric acid and alkali metal fluorides[18,19]. Ipatieff and Grosse[20] patented a method of alkylating three- and four-membered cycloalkanes with propene and butene in the presence of sulphuric and phosphoric acids, zirconium chloride, boron trifluoride, and activated clay. According to Levitt's data, the reaction of cyclopropane with t-butyl chloride in the presence of aluminium chloride results in the formation of a mixture of products having the composition $C_7H_{15}Cl$.[21,22]

In the presence of acid catalysts six-membered alkylcycloalkanes react with alkenes more readily than the unsubstituted compounds, forming the corresponding dialkylcycloalkanes. In the alkylation of alkylcyclopentanes the ring isomerises to a six-membered ring, and products of direct alkylation are not observed in the alkylation mixture.

According to the data of Ipatieff et al.[23], ethylene reacts with methylcyclohexane and methylisopropylcyclohexane in the presence of aluminium chloride (70°, 15 atm) and also with methylcyclohexane and methylcyclopentane in the presence of boron trifluoride (30°, 15 atm).

The alkylation of methylcyclopentane with propene in the presence of aluminium bromide at -42° was studied by Pines and Ipatieff[24]. Alkylated cyclohexane with the composition C_9H_{18} and other hydrocarbons with the composition $C_{12}H_{22}$ were isolated. The hydrocarbon C_9H_{18} proved to be 1-ethyl-2-methylcyclohexane, which is formed by the following mechanism:



The structures of 1-cyclohexyl-3-methylcyclopentane and 1-cyclohexyl-2-methylcyclopentane were attributed to the hydrocarbons with the composition $C_{12}H_{22}$. However, in later studies it was shown that these hydrocarbons consist of a mixture of 2,3- and 2,6-dimethyldecalins[25,26].

In 1944 Pines and Ipatieff patented a method of alkylating methylcyclopentane with propene in the presence of phosphoric acid at 100–400°[27] or boron trifluoride promoted by hydrofluoric acid at 30–50°.[28]

In the alkylation of methylcyclopentane with butenes, pentenes, and octenes in the presence of sulphuric and hydrofluoric acids, direct alkylation products could not be detected in the catalytic reaction mixture[29-31]. The authors of these studies explained their results by postulating that the main reaction is accompanied by a number of side-processes, such as the expansion of five-membered rings, dehydrogenation of cycloalkanes and hydrogenation of alkenes, isomerisation of alkenes with subsequent hydrogenation to isoalkanes, depolymerisation and dealkylation, and dehydrogenation of cycloalkanes with formation of polycyclic hydrocarbons.

The main product of the alkylation of methylcyclopentane with butene in the presence of sulphuric acid at 10–17° is a mixture of 1-ethyl-3,5-dimethyl- and 1-ethyl-3,4-dimethyl-cyclohexanes (83%). In the alkylation of methylcyclopentane with isobutene under the same conditions 10% of alkylated cyclohexane and 31% of polycyclic compounds were obtained. In the alkylation of methylcyclopentane with di-isobutene 4% of alkylcyclohexane and 60% of di- and poly-cyclic hydrocarbons were formed. Pent-2-ene enters into the reaction with greater difficulty than but-1-ene. Alkylated cycloalkanes, isopentane, decanes, and polycyclic hydrocarbons were obtained in the alkylation of methylcyclopentane with 3-methylbut-1-ene.

In the presence of hydrofluoric acid at 10° methylcyclopentane almost does not react with but-1-ene. When the reaction temperature was raised to 60°, alkanes, 1-ethyl-2,4-dimethylcyclohexane, and dicyclic hydrocarbons were isolated.

Schneider[32] alkylated methylcyclopentane, dissolved in isobutane or isopentane, with propene and isobutene in the presence of hydrofluoric acid. The main reaction product was tetramethylcyclohexane. Under similar conditions methylcyclohexane does not react either with isobutene or but-2-ene. The main product of the alkylation of methylcyclohexane with propene in the presence of aluminium chloride was a mixture of 1-methyl-3-propyl- and 1-methyl-4-propyl-cyclohexanes; polymethylated cyclohexanes were not detected.

Chernevskaya[33] showed that in the alkylation of methylcyclohexane with octyl chloride over a period of 6 h at 90° in the presence of aluminium chloride *gem*-methyloctylcyclohexane forms in 30% yield. Schmidl's patent[34] deals with the preparation of synthetic lubricating oils by the reaction of cycloalkanes with olefins in the presence of aluminium chloride.

Aluminium chloride has been suggested as the catalyst for the alkylation of methylcyclohexane with alkyl halides at 20–80°. A small amount of chlorocyclohexane forms together with alkylcyclohexanes[35]. Ethylmethylcyclohexane was obtained in the alkylation of methylcyclohexane with ethylene over a period of 6 h at 160–195° and a pressure of 65 atm. Mixtures of thorium oxide, aluminium chloride, and a metal (magnesium, sodium, or aluminium) have been recommended as catalysts for the process[36].

In the reaction between methylcyclohexane and ethylene in the presence of a mixture of stannous chloride and aluminium chloride a mixture of ethylmethylcyclohexane, trimethylcyclohexanes, and tetramethylcyclopentanes is formed. In the absence of aluminium, there is virtually no alkylation[37]. For the alkylation of methylcyclohexane with propene, Appell[38] proposed a mixed catalyst consisting of aluminium chloride and aluminium with added iron, cobalt, nickel, or tin. 1-t-Butyl-4-methylcyclohexane was obtained in the reaction between methylcyclohexane and isobutene at 0–25° in the presence of sulphuric acid[39]. McAllister and Bullard[40] alkylated alkylcycloalkanes with cyclopentene and cyclohexene in the presence of sulphuric acid promoted with benzenesulphonic acid or a mixture of sulphuric and phosphoric acids. In a study of the alkylation of methylcyclohexane with propene in the presence of sulphuric acid, Mamedaliev and Kuliev[41] showed that, in contrast to paraffinic hydrocarbons, the hydrogen of the tertiary carbon atom of methylcyclohexane is not substituted by an alkyl group: the catalytic reaction mixture does not contain *gem*-disubstituted cycloalkanes. In the alkylation of methylcyclohexane, ethylcyclohexane, and isopropylcyclohexane with propene and isobutene in the

presence of sulphuric acid at 0–60° up to 20–30% of dialkylcyclohexanes is formed, mainly 1,4-isomers, and 15% of polyalkylcyclohexanes[12,13]. Thus in the reaction between methylcyclohexane and propene 1-isopropyl-4--methylcyclohexane was obtained.

Unlike the other substituted cyclohexanes investigated, t-butylcyclohexane is not alkylated by alkenes in the presence of sulphuric acid, which may be due to steric hindrance caused by the t-butyl group.

In the alkylation of methyldecalin with propene in the presence of sulphuric acid[42,43], it was found that under the optimum conditions (30° and molar ratios sulphuric acid : methyldecalin : propene = 2 : 1 : 1) the alkylation mixture contains 20% of isopropylmethyldecalin. In the reaction between decalin and ethylene in the presence of aluminium chloride[44], a reaction mixture of complex composition was obtained from which it proved possible to isolate only a small amount of 2-ethyldecalin.

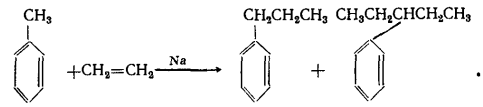
Chernevskaya[33] studied the alkylation of decalin with alkyl halides in the presence of aluminium chloride at 100°. A study was made of the effect of temperature, duration of the reaction, amount of catalyst, and the proportions of the reactants. As the amount of catalyst was increased, there was an increase in the yield of the reaction products but the content of the desired product fell. With the increase in the decalin : alkyl halide ratio from 1 : 1 to 10 : 1, the yield of alkyl derivatives increased to 30%. The maximum yield of the alkylation products was obtained in the presence of 2% of catalyst. The main products of the reaction are disubstituted derivatives.

The alkylation of aromatic compounds in the presence of acid catalysts is well known[45,46]. In the presence of acid catalysts, aralkanes are alkylated in the ring. A study has been made of the ethylation of toluene in the presence of mixed catalysts. Only traces of *p*-propylbenzene and 3-phenylpentane are formed at 300° on an aluminium–chromium catalyst. In the presence of an aluminium–molybdenum or an aluminium–cobalt–molybdenum catalyst the ring is alkylated. Both types of alkylation are observed to a small extent in the presence of an aluminium–platinum catalyst. In all cases the ethylene was also polymerised[47].

Much work has been done on the alkylation of tetralin, which, as regards its properties, can also be classified as an aralkane. The catalysts used in these reactions were phosphoric[48], hydrofluoric[49], and sulphuric[50] acids, aluminium[51], aluminosilicate[52], aluminium chloride[50], zinc chloride[52], etc. It has been established that in the presence of acid catalysts only the aromatic ring is alkylated.

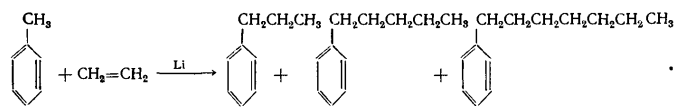
3. ALKYLATION OF ARALKANES IN THE PRESENCE OF BASIC CATALYSTS

In 1928 Hofmann and Michael[53] showed that aliphatic aromatic hydrocarbons can be alkylated by diolefins in the presence of alkali metals and their alloys. The alkylation of toluene and tetralin with butadiene in the presence of sodium was described as an example. Later Whitman[54] showed that aliphatic-aromatic hydrocarbons (toluene, cumene, tetralin) and unsaturated cyclic compounds (cyclohexene, cyclopentadiene) can be alkylated at 150–450° and a pressure of 50–3000 atm in the presence of 0.1–2% of an alkali metal. Thus in the alkylation of toluene with ethylene over a period of 17 h at 225° in the presence of sodium, n-propylbenzene and 3-phenylpentane were obtained:



The alkylation of ethylbenzene with styrene in the presence of sodium[57] gave 1,3-diphenylbutane as the main product. It has been established[55,56] that the yield of the monoalkylated derivative increases on addition of powdered iron. Pieper and Wegler[58,59] extended this reaction to nitrogen--containing heterocycles (picoline, quinaldine, 2-methylbenzothiazole). In the reaction of 370 g of picoline with 200 g of butadiene in the presence of 7 g of sodium over a period of 1 h at 100–120° 160 g of the monoalkenyl derivative and 100 g of the dialkenyl derivative was obtained.

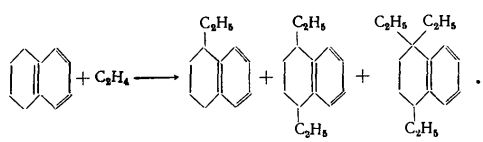
Fotis[60] showed that in the presence of lithium alkylation takes place at the terminal carbon atom of the side-chain of aliphatic-aromatic hydrocarbons. For example, in the alkylation of toluene (0.47 mole) with ethylene (68 atm) in the presence of lithium (0.075 mole) for 25 h at 250° 40% of n-propylbenzene, 13.4% of 1-phenylpentane, 13.4% of 1-phenylheptane, and 33.2% of a residue was obtained:



Later it was shown that the alkylation of the side chain of aliphatic-aromatic hydrocarbons can be carried out in the presence of organic alkali metal compounds. Little[61] alkylated toluene, tetralin, and cyclohexene in the presence of pentylsodium and phenylsodium.

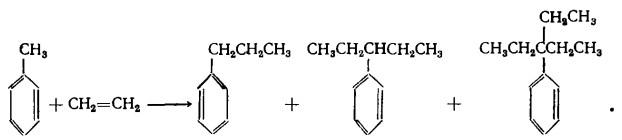
Pines and Ipatieff showed that the side chain of alkylbenzenes can be alkylated with alkenes in the presence of alkali metal acetylides[62], a mixture of an alkali metal and a nitrogen-containing compound[63], a mixture of alkali metals and an organic peroxide, and a mixture of an alkali metal and an organic compound of the general formula RX, where R = alkyl, alkenyl, cyclohexyl, and alkylphenyl, and X = OH, COOH, OR, NO_2, Cl, and CN[64–67]. Sodioanthracene proved to be the best catalyst.

Glosson et al.[68–72] alkylated cyclohexene, tetralin, toluene, and alkylheterocycles with alkenes in the presence of benzylsodium and sodiotetralin. Thus in the alkylation of cyclohexene with ethylene for 2.5 h at 125° in the presence of benzylsodium, 9.6% of 3-ethylcyclohexene was obtained. Under similar conditions isobutylbenzene was prepared from toluene and propene. The alkylation of tetralin was carried out in the presence of sodiotetralin at 140° and an ethylene pressure of 100 atm. The reaction yielded 21% of 1-ethyltetralin, 41% of 1,4-diethyltetralin, and 8% of 1,1,4-triethyltetralin:



Pines et al.[73] alkylated toluene, ethylbenzene, propylbenzene, indane, and cyclohexylbenzene with ethylene in

the presence of sodioanthracene at 200–225° and a pressure of 30 atm. The alkylation of toluene gave *p*-propylbenzene, 3-phenylpentane, and 3-ethyl-3-phenylpentane:



Ethylbenzene reacts with ethylene to form s-butylbenzene (75%) and a small amount of 3-methyl-3-phenylpentane. The reaction of isopropylbenzene with ethylene gives t-pentylbenzene (78%). t-Butylbenzene does not react with ethylene. In the alkylation of cyclohexylbenzene, 1-ethylphenylcyclohexane was obtained (50%) while the alkylation of indane yielded 1-ethylindane (26%). It has been found that the reactivity of xylenes in the alkylation reaction decreases in the series *o*-xylene > *m*-xylene > *p*-xylene. The reaction with ethylene gives between 66 and 80% of the corresponding n-propyltoluenes. Cymene gives 62% of the monoalkylated derivatives which contain 72% of *p*-t-pentyltoluene. The alkylation of mesitylene gave 79% of 1,3-dimethyl-5-n-propylbenzene.

It has been shown, using the alkylation of toluene with ethylene as an example, that compounds which readily react with sodium, for example anthracene, fluorene, *o*-chlorotoluene, *o*-bromotoluene, and peroxides are satisfactory promoting agents.

According to a number of investigators, the mechanism of the alkylation of aliphatic-aromatic hydrocarbons, for example toluene, can be represented as follows (RX = molecule of promoting agent, X = halogen):

$$RX + 2Na \rightarrow RNa + NaX, \quad (1)$$

$$C_6H_5CH_3 + RNa \rightarrow C_6H_5CH_2Na + RH, \quad (2)$$

$$C_6H_5CH_2Na + CH_2{=}CH_2 \rightarrow C_6H_5CH_2CH_2CH_2Na, \quad (3)$$

$$C_6H_5CH_2CH_2CH_2Na + C_6H_5CH_3 \rightarrow C_6H_5CH_2CH_2CH_3 + C_6H_5CH_2Na, \quad (4)$$

$$C_6H_5CH_2Na + C_6H_5CH_2CH_2CH_3 \rightarrow C_6H_5CH_3 + C_6H_5CH(Na)CH_2CH_3, \quad (5)$$

$$C_6H_5CH(Na)CH_2CH_3 + CH_2{=}CH_2 \rightarrow C_6H_5CH\langle{}^{CH_2CH_3}_{CH_2CH_2Na}, \quad (6)$$

$$C_6H_5CH\langle{}^{CH_2CH_3}_{CH_2CH_2Na} + C_6H_5CH_3 \rightarrow C_6H_5CH(C_2H_5)_2 + C_6H_5CH_2Na. \quad (7)$$

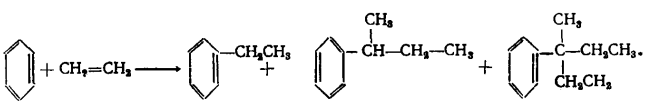
The reaction of promoting agents with sodium gives organosodium compounds which metallate the side-chain of the aliphatic-aromatic hydrocarbon. The resulting organosodium compound adds to ethylene with formation of a new organosodium compound which then metallates the initial hydrocarbon or the ethylated alkylbenzene, forming the monoalkylation product.

Later Pines and Mark[74] studied the reaction of aliphatic-aromatic hydrocarbons with various olefins in the presence of organosodium compounds at 300°. They showed that the reaction of but-1-ene and oct-1-ene gives 2-benzylbutane and 2-benzyloctane in up to 10% yields. Similarly the reaction of propene with toluene, ethylbenzene, isopropylbenzene, and diphenylmethane results in the formation of isobutylbenzene (10%), 3-methyl-2-phenylbutane (16.7%), 2,3-dimethyl-2-phenylbutane (7.8%), and 2-methyl-1,1-diphenylpropane (51%) respectively. 1,3-Diphenylpropane (21%), 1,3-diphenylbutane (12%), 1,3,5-triphenylpentane (29%), and 1,3,5-triphenylhexane (16%) are formed in the alkylation of toluene and ethylbenzene with styrene[75] in the presence of sodium at 110–125°. The yield of monosubstituted derivatives increases in the presence of promoting agents: benzylsodium, sodioanthracene, and sodium isopropoxide. For example, in the case of benzene the yield of monoalkyl derivatives increases from 21 to 40%. In the presence of promoting agents isopropylbenzene reacts with styrene, forming 9% of monoalkylated and 29% of dialkylated derivatives; in the absence of promoting agents polymers are formed.

Schaap and Pines[76] studied the alkylation of toluene, ethylbenzene, cumene, and cyclohexylbenzene with ethylene in the presence of the potassioanthracene catalyst. Cyclisation products were found in the catalytic reaction mixture together with monoalkyl derivatives. The yield of cyclisation products ranges from 2% for toluene to 43% for cumene. Addition of sodium to potassioanthracene increases the yield of alkylation products.

The reaction of isopropylbenzene with ethylene in the presence of metallic potassium gives only the alkylation product[77]. It is interesting that a mixture of potassium hydride and butyl-lithium is an active catalyst for both alkylation and cyclisation of the side-chain of aliphatic-aromatic compounds[78].

Podall and Foster[79] state that the toluene side-chain may be alkylated in the presence of graphite–potassium alloy. According to the data of Esmay et al.[80], in the presence of alkali metals on carriers benzene is alkylated with subsequent further alkylation of the side chains. Thus in the reaction of benzene with ethylene in the presence of Na/Al_2O_3 the products obtained were 10% of ethylbenzene, 40% of s-butylbenzene, and 30% of 3-methyl-3-phenylpentane:



Other catalysts which may be used are Na/C and Li/C and also potassium, sodium, lead, and caesium on MgO, ZnO, BaO, and CdO.[81] The alkylation does not take place in the presence of Na/NaCl and Na/TiO_2.

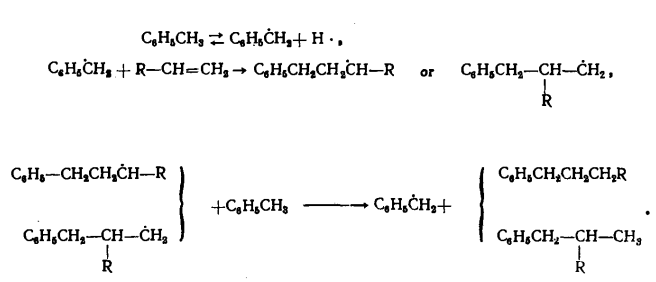
In many cases the alkylation of aliphatic-aromatic and unsaturated cyclic hydrocarbons can be achieved in the presence of alkali metal hydrides[82,83]. Thus Voltz[47] showed that the reaction of toluene with ethylene in the presence of sodium and lithium hydrides at 300° gives alkylation and polymerisation products. In the presence of calcium, strontium, and barium hydrides there is no alkylation. The hydrides of titanium and tantalum are ineffective in the alkylation of toluene at 300°. In the presence of zirconium hydride there is both alkylation of toluene and polymerisation of the alkene.

4. THERMAL AND INITIATED ALKYLATION OF CYCLOALKANES, OXACYCLOALKANES, AND ARALKANES

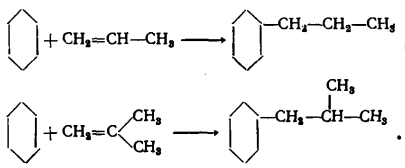
The side-chains of aliphatic-aromatic compounds are known to resemble in their chemical properties alkanes and therefore it might have been expected that it would prove possible to alkylate the side-chains of such hydrocarbons without involving their aromatic rings. Acid catalysts are unsuitable for this purpose, since in their presence the aromatic ring is in fact alkylated. By analogy with the behaviour of alkanes, Ipatieff et al.[84] attempted to

alkylate the side-chain of alkylbenzenes at a high temperature and pressure. It was shown that the alkylation of toluene with ethylene gives n-propylbenzene.

Subsequently this reaction was studied by Pines and coworkers[85-87]. The thermal alkylation of toluene (I), ethylbenzene (II), and cumene (III) was studied in a flow system at a pressure of 420 atm and 400–500° using a brief contact time and a molar ratio alkylbenzene : alkene of 5 : 1. As was expected, an asymmetric alkene gives two products, corresponding to addition to two different carbon atoms of the double bond. One of the products is formed in a greater amount, as happens in the alkylation of alkanes. The authors introduced the concept of "selectivity", i.e. the ratio of the yield of the product of addition to the more stable radical and the yield of the product of addition to the less stable radical. It was shown that the selectivity of addition of alkylphenyl groups to asymmetric alkenes decreases with decrease in the stability of the corresponding free radical. As in the thermal alkylation of alkanes, the reactivity of alkenes decreases in the series propene > > isobutene > 2-methylbut-2-ene, but-1-ene > but-2-ene. A free-radical mechanism, similar to that for the thermal alkylation of alkanes, was proposed for the formation of the monoalkylation products:



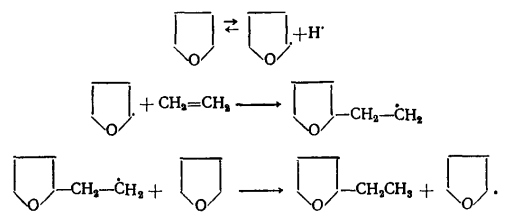
Recently the alkylation of cyclohexane[88] and cyclopentane[89] with alkenes was achieved at 450° at a pressure of 200 atm. Ethylcyclohexane, propylcyclohexane, and isobutylcyclohexane were isolated in the alkylation of cyclohexane with ethylene, propene, and isobutene respectively. It was found that at an elevated temperature cyclohexane adds to the most unsaturated carbon atom of the alkene:



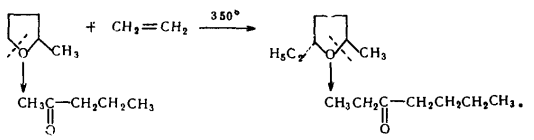
Study of the alkylation of methylcyclohexane with alkenes[90] at 350° and 50 atm showed that the main product of the reaction of methylcyclohexane with ethylene is a mixture of ethylmethylcyclohexanes. The reaction with propene proceeds with greater difficulty. Since it is known that a tertiary radical forms more readily than a secondary radical, it might have been expected that the alkylation of methylcyclohexane with ethylene would give 1-ethyl-1-methylcyclohexane. However, a mixture of 1-ethyl-3-methyl- and 1-ethyl-4-methyl-cyclohexanes was obtained instead.

In contrast to benzene, cyclohexane reacts with alkenes albeit at an elevated temperature and pressure. The different behaviour of cyclohexane and benzene in the alkylation process is shown clearly in the alkylation of tetralin. It might have been supposed[91] that under similar conditions tetralin should be selectively alkylated by olefins in the cycloparaffin ring, and this was confirmed experimentally. 1-Ethyltetralin and 1,4-diethyltetralin were isolated after alkylation of tetralin with ethylene at 450° and 200 atm; the alkylation with propene proceeds with greater difficulty.

In their study of the reaction of oxacycloalkanes (tetrahydrofuran, tetrahydrosilvan, tetrahydropyran) with various olefins at an elevated temperature, Shuikin and Lebedev[92] found that alkylation occurs in the temperature range 300–400°; below 300° there is virtually no reaction and above 400° decomposition processes predominate. A study was made of the effect of temperature, the duration of the reaction, and ethylene pressure on the degree of conversion of the oxacycloalkanes and the yield of monoalkyl derivatives. It is interesting that introduction of a methyl group into the tetrahydrofuran ring lowers the yield of the monoalkyl derivative. Apparently thermal alkylation of oxacycloalkanes, for example tetrahydrofuran, takes place by a free-radical mechanism, like the thermal alkylation of alkanes:



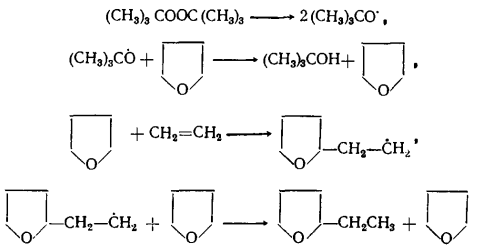
In their oxacycloalkane alkylation experiments, Shuikin and Lebedev[93] were the first to observe the thermal isomerisation of alkyl tetrahydrofurans. 2-Pentanone (the product of the isomerisation of the initial tetrahydrosilvan) and 3-heptanone (the product of the isomerisation of the 2-ethyl-5-methyltetrahydrofuran formed) were detected in the products of the alkylation of tetrahydrosilvan with ethylene at an elevated temperature:



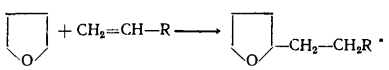
Ethylene is known to undergo polymerisation in the presence of peroxides[94], the rate of polymerisation increasing appreciably in the presence of ethers[95]. A number of patents describe the formation of polymerisation products in the reaction of cyclic ethers with unsaturated compounds. For example, the formation of heavy waxes in the telomerisation of ethylene with dioxan, tetrahydrofuran, dioxolane, and ethyl ether at 50–300° and a pressure of 400–1000 atm has been described[96].

According to the data of Hanford and Roland[97], the reaction of oxygen-containing compounds with ethylene in the presence of radical-forming initiators gave polymerisation products with the formula $R(CH_2CH_2)_nH$, where n is between 22 and 54. In particular, the reaction of dioxan with ethylene resulted in the formation of a product having the formula $C_4H_8O_2(CH_2CH_2)_{54}H$. The telomerisation of dioxolane with ethylene (600–900 atm) for 18 h at 100° in the presence of benzoyl peroxide yielded a wax having the composition $C_3H_6O_2(CH_2CH_2)_{44.5}H$.[98] The products of the reaction of dioxan with decene in the presence of benzoyl peroxide are used as lubricating oils[99].

Shuikin and Lebedev[100] showed that in the presence of di-t-butyl peroxide the reaction of oxacycloalkanes with unsaturated compounds occurs at a much lower temperature (150°). The radical mechanism of the alkylation and the initiating activity of peroxides is confirmed by the presence in the reaction products of t-butanol, which is formed as follows:



Using the alkylation of tetrahydrofuran and tetrahydropyran with hex-1-ene as an example, it was shown that a decrease of the concentration of the alkene results in an increase of the yield of the monoalkyloxacycloalkane. Thus when the tetrahydrofuran : hex-1-ene ratio is increased from 10 : 5 to 10 : 0.5, the yield of 2-hexylhydrofuran increases from 13.2 to 79.2%.[101,102] An increase of the length of the hydrocarbon chain of the alkene lowers somewhat the yield of the 2-alkyloxacycloalkane. The corresponding 2-ethyloxacycloalkanes were obtained in the alkylation of tetrahydrofuran, tetrahydropyran, and dioxan with ethylene in the presence of peroxide at 150°. In the presence of peroxide the alkene adds to oxacycloalkanes via its most unsaturated carbon atom. Thus in the alkylation of tetrahydrofuran with propene, hex-1-ene, hept-1-ene, and oct-1-ene in the presence of peroxide the corresponding 2-alkyltetrahydrofurans with a straight side-chain were obtained:



A similar situation is observed in the alkylation of tetrahydropyran with hex-1-ene and hept-1-ene.

According to Schmerling's data[103], in the presence of organic peroxides cycloalkanes interact with ethylene and form polymers. For example a polymer having the composition $C_6H_{11}(CH_2-CH_2)_nH$ was obtained in the reaction between cyclohexane and ethylene. It has been stated[104] that ethylene enters into a telomerisation reaction with toluene at 200° and a pressure of 140 atm when the process is initiated with cumenyl hydroperoxide.

Nikishin et al.[105] established that toluene, ethylbenzene, cumene, *p*-xylene, and α-methylnaphthalene are capable of adding to alkenes at 150–160° in the presence of t-butyl peroxide. The yield of the monoalkylation products is 10–15%. In the presence of tetraethyl-lead alkylbenzenes are alkylated by ethylene at the α-carbon atom of the side-chain[106].

Eidus and Ershov[107,108] showed that when mixed with carbon monoxide and hydrogen cyclohexene is methylated to the extent of 7–10% by CH_2 radicals formed on reduction of the carbon monoxide with hydrogen, and is converted into mono- and 1,2-di-methyl derivatives. Methylcyclohexene was also obtained in the alkylation of cyclohexene by methylene radicals formed by the hydrocracking of isobutene at 190° on a cobalt–clay catalyst[109].

The review of the literature dealing with the alkylation of saturated cycloalkanes shows that, in the presence of acid catalysts, the composition of the alkylation products depends on the structure of the cycloalkane and the nature of the catalyst. Thus in the presence of aluminium chloride, unsubstituted cyclohexane forms a mixture of polymethylated cyclohexanes. In the presence of sulphuric acid neither cyclopentane nor cyclohexane reacts with alkanes.

In the alkylation of alkylcyclopentanes in the presence of aluminium chloride or boron trifluoride expansion to a six-membered ring takes place; direct alkylation products have not been detected in the alkylation mixture. In the presence of sulphuric acid six-membered alkylcycloalkanes form the corresponding 1,4-dialkylcyclohexanes. In the alkylation of tetralin in the presence of acid catalysts the alkylating agent adds to the aromatic ring; under these conditions the cycloparaffin ring is not alkylated.

The study of the alkylation of saturated systems entered a new phase when it was found that the alkylation of cycloalkanes and the side-chain of aliphatic-aromatic compounds can be carried out in the presence of basic catalysts: sodium, sodioanthracene, benzylsodium, potassium, lithium, etc. Thus in the alkylation of toluene with ethylene in the presence of sodium propylbenzene is obtained and in the alkylation of tetralin in the presence of sodiotetralin ethylene adds to the cycloparaffin ring.

The need to obtain motor fuels with a higher octane number led investigators to attempt the thermal alkylation of alkanes. An industrial method has been developed for the preparation of neohexane by the thermal alkylation of isobutene with ethylene. Subsequently, assuming an analogy with the behaviour of alkanes, a study was made of the thermal alkylation of the side-chains of aliphatic-aromatic hydrocarbons, cycloalkanes, and oxacycloalkanes. The alkylation of the side-chains of aliphatic-aromatic hydrocarbons and oxacycloalkanes occurs under milder conditions in the presence of initiating substances. Chloroform, benzyl chloride, dichloropropane, and organic peroxides have been suggested as initiators.

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OUTER-SPHERE INTERACTION IN AQUEOUS SOLUTIONS OF COMPLEX COMPOUNDS

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1. INTRODUCTION

The majority of chemical processes in nature and technology take place in aqueous solutions. These processes are closely linked with complex formation.

Ions in water are present as simple aquo-ions or mixed complexes: hydroxoaquo-, oxoaquo-, halogenoaquo-, and similar compounds. Complex formation in solutions involves the replacement of ligands in the inner sphere of the so called "free" central ion. This replacement may take place with or without change in the geometric configuration of the inner sphere[1,2].

Complex compounds in solution are defined as any associated species whose components are joined by a direct bond[3], whose energy of formation is greater than, or at least only slightly less than, the kinetic energy of the solvent molecules[4]. Associated species in which there is no direct bond between the ions are called outer-sphere complexes or associated species of the ion-pair type[5].

The results of many studies[3] show that complex formation in solutions is not restricted to the Werner[6] coordination sphere. Complex ions which according to Werner's theory are coordinatively saturated may still combine with ions with opposite sign[3] and polar molecules[7].

In a number of complexes the stability of the inner-sphere bonds is comparable to and even slightly less than the stability of the outer-sphere bonds[3,8,9]. This situation is often encountered in complex formation in concentrated ($> 1\ N$) aqueous solutions of inert salts, but is sometimes also found in dilute aqueous solutions of complex compounds[10,11].

Data have been published on outer-sphere interaction in aqueous solutions of complex compounds in the presence and absence of inert salts, but there are no reviews or monographs on this subject. Moreover, technologists and many research workers, following Bjerrum[12], consider that the influence of outer-sphere ions on complex formation in aqueous solutions is non-existent or negligibly small relative to the effect of inner-sphere interaction, although there are not always sufficient grounds for this.

The present paper is an attempt to examine critically published data on outer-sphere interaction in aqueous solutions of complex compounds. The problem of standardising conditions for the study of outer-sphere association is discussed, a procedure for calculating outer-sphere association constants for labile[13] and relatively unstable ionic

complexes is described, it is shown that outer-sphere association obeys the law of mass action, and the chief methods for studying outer-sphere interaction are described. In addition, a number of new regular features of outer-sphere association are formulated, the stabilities of outer-sphere and inner-sphere bonds in various complexes are compared, the possibility of predicting outer-sphere association constants in certain systems which have not been studied is demonstrated, and complex formation with allowance for associative interaction of the ions with the salt medium is discussed.

2. STANDARDISATION OF CONDITIONS FOR STUDYING OUTER-SPHERE ASSOCIATION IN AQUEOUS SOLUTIONS OF COMPLEX COMPOUNDS

Outer-sphere association in aqueous solutions of complex compounds is studied under the same standard conditions as the inner-sphere interaction[14,15]. The chief standard state for the study of complex formation in solutions is a hypothetical molal solution exhibiting the properties of an infinitely dilute solution[16]. In addition, in the past twenty years the state of solutions with high and constant ionic strength has been taken as standard state[15-18].

The low stability of outer-sphere complexes makes it impossible to obtain accurate values for their thermodynamic functions relating to an infinitely dilute solution, due to the difficulty of graphical or analytical extrapolation of the low values of the thermodynamic functions from real concentrated solutions to solutions with zero ionic strength[14].

Vasil'ev's work[19,20] improved the procedure for extrapolating the stability constants of ionic complexes to zero ionic strength. Vasil'ev replaced the two [adjustable ? (Ed. of Translation)] constants in the Debye–Hückel equation[21] by a single constant (the ion parameter a) and assumed that this constant has the value 4.9 Å in all systems. This assumption is hardly justified for all types of outer-sphere complexes, for which the ion parameter a may vary over a wider range than for ionic complexes.

The most convenient standard state for the study of outer-sphere association in labile and relatively unstable (first stability constant less than 100) ionic complexes is that of solutions with high and constant ionic strength[15] maintained with inert salts. The use of lithium perchlorate as an inert salt is recommended[3], since the ClO_4^- anion and Li^+ cation form the least stable associated species with the majority of singly-, doubly-, and triply-charged ionic complexes[22]. Ions with a lower tendency to undergo association than for example the ClO_4^- anion are known[23] but they are unfortunately unstable in aqueous solutions.

The Li^+ cation cannot be used as an inert ion in systems with anionic complexes whose charge exceeds three. On association, highly-charged ionic complexes break down the hydration sheath of the Li^+ cation and form more stable associated species with this cation than with the cations of the other alkali metals. Large cations of the type NR_4^+, where R = CH_3, C_2H_5, etc.[24,25], are inert with respect to highly-charged anionic complexes. The majority of salts with NR_4^+ cations are sparingly soluble in water, so that the outer-sphere association of highly-charged ionic complexes is usually studied[22] in dilute solutions with variable or constant ionic strengths and the thermodynamic functions are calculated for solutions with zero ionic strength. The hypothetical molal solution exhibiting the properties of an infinitely dilute solution can be used as a standard state for the study of the outer-sphere association of highly-charged ionic complexes, since the latter form extremely stable outer-sphere complexes.

If lithium perchlorate is used as an inert salt to establish the ionic strength, outer-sphere association is studied[3] in solutions with ionic strengths equal to three or four, since the low stability of the outer-sphere complexes necessitates high concentrations of outer-sphere ions for their formation, and in solutions with low ionic strengths this leads to a change in the activity coefficients of the reacting components. Studies in lithium perchlorate solutions with concentrations greater than 4 M are impossible, since the solubility of lithium perchlorate in water at 20° is 4.2 M.

The replacement of water by aqueous solutions of inert salts does not alter the significance of the laws of thermodynamics[18], so that solutions with high and constant ionic strengths and the hypothetical molal solution exhibiting the properties of an infinitely dilute solution can equally justifiably be regarded as standard states. Change from one standard state to the other changes the conditions under which the activity coefficients are equated to unity. Change in the conditions changes the composition of the associated species which include both "free" ions and ionic complexes[17].

In dilute aqueous solutions the concentration of free ions M (here and subsequently the charges of most ions are omitted for simplicity) is understood to be the concentration the species $\sum_{n=0}^{n=N} M(H_2O)_n$, where N is the maximum number of water molecules joined to M. X-Ray study of aqueous solutions[26], study of exchange with water containing the isotope ^{18}O,[27] magnetic and spectroscopic data[28], and their interpretation[29] from the viewpoint of ligand field theory show that in dilute aqueous solutions of most completely dissociated salts, N is the maximum coordination number of Werner's theory.

In concentrated solutions of inert salts, for example in lithium perchlorate solutions, the concentration of free M ions is understood to be the total concentration of associated species:

$$\sum_{x=0}^{x=X}\sum_{y=0}^{y=Y}\sum_{z=0}^{z=Z} M(H_2O)_x(ClO_4)_yLi_z, \qquad (1)$$

and the concentration of ionic complexes ML_n, where L is the ligand, is understood to be the concentration of the species

$$\sum_{n=0}^{n=N}\sum_{x=0}^{x=X}\sum_{y=0}^{y=Y}\sum_{z=0}^{z=Z} ML_n(H_2O)_x(ClO_4)_yLi_x \qquad (2)$$

where n lies in the range $1-N$. There is at present no information on the values of X, Y, and Z in species of types (1) and (2).

Outer-sphere associated species made up of ionic complexes of low stability have been studied chiefly in 3 M and 4 M $Li(ClO_4, L)$ and (Li, B)L solutions[3,8,9,30-46], where B represents the outer-sphere ions. The concentration of ligand in $Li(ClO_4, L)$ solutions was varied in a number of systems in the range 0–3 M and 0–4 M.

The replacement of any quantity of perchlorate or other inert anions by ligand anions leads unavoidably to a change in the activity coefficients of the reactant and product ions

in solutions with high and constant ionic strength[47]. However, the activity coefficients of M, L, and ML_n are assumed[15,17,35,36,48] to be constant in 1–4 M Li(ClO_4, L) and Na(ClO_4, L) solutions for replacement of less than 10–15% of the perchlorate ions by singly-charged ligand anions, since the low accuracy of present experimental methods does not permit a change in activity coefficients to be observed under the above conditions. The replacement of more than 20% of the perchlorate anions by ligand anions produces a significant change in the activity coefficients of the reacting ions in the great majority of systems studied in 1–4 M Li(ClO_4, L) and Na(ClO_4, L) solutions, the logarithms of the activity coefficients being directly proportional to the logarithms of the ligand anion concentrations[3,49,50].

The extent of the change in the activity coefficients of M and L in solutions with high (greater than 0.1 M) and constant ionic strength is influenced markedly by the nature of the reacting ions[3,15,48]. The extent of this change is often determined[15,35,36,48] from the deviation from constant values shown by $a_M j+[L^-]^j$ or $[M^{j+}]a_{L^-}$ (a is the activity†) for sparingly soluble salts containing M and L, in solutions saturated with such salts. These data indicate that increase in the charge of M or in the differences between the electrostatic characteristics of L and the inert anion leads to an increase in the deviations of the activity coefficients of M and L from constant values. For example, the complete replacement of perchlorate anions by chloride, bromide, thiocyanate, and iodide anions in 4 M Na(ClO_4, L) solutions at 25° alters the value of $a_{Tl^+}[L^-]$, which changes in the same sense as the activity coefficients of M and L, by 36, 12, 9, and 3% respectively[48]. $a_{Tl^+}[L^-]$ changes to almost the same extent when ClO_4^- is replaced by L in 4 M Li(ClO_4, L) solutions[3,15]. The values of $a_{Pb^{2+}}[L^-]^2$ in 3 M and 4 M Li(ClO_4, L) and Na(ClO_4, L) solutions change by 74% and 35% on complete replacement of perchlorate anions by chloride and bromide ions respectively[3,35].

The nature of the alkali and alkaline earth metal cations has little influence on the values of $a_M j+[L^-]^j$ in 3 M and 4 M (Li, B)L solutions, where B represents alkali and alkaline earth metal cations[15,35,36]. It may be assumed[3] that the replacement of Li^+ cations by B cations alters the values of $[M^{j+}]a_{L^-}$, but there is no published information on these quantities.

One of the main disadvantages of both standard states (the hypothetical molal solution and solutions with high and constant ionic strength) used in the study of the stability of ionic and outer-sphere complexes is the change in the activity coefficients of the reacting ions with change in the salt composition of the medium being studied. In solutions with high and constant ionic strength the activity coefficients are more nearly constant than in solutions with varying ionic strengths. It is, however, easier at present to make allowance for the change in the activity coefficients in dilute (< 0.2 N) solutions with varying ionic strength than in solutions with high and constant ionic strength. The values of the thermodynamic functions for relatively unstable associated species cannot be determined with high accuracy whatever method is used to allow for activity coefficients[3].

The advantages and disadvantages of the standard states for studying equilibria in aqueous solutions have been discussed many times[3,5,15,17,18]. The great majority of accurate studies of equilibria in solutions have been made in the past twenty years[22] by the constant ionic strength method[51] and the self-medium method[52]. Where possible, equilibria should be studied in solutions at several constant ionic strength values, after which various methods should be used to calculate the values of the thermodynamic functions for solutions with zero ionic strength. This applies equally to the thermodynamic functions of ionic[20] and outer-sphere complexes[20]. An unambiguous comparison of the thermodynamic functions of standardised solutions with the same high and constant ionic strength can be made only when the same inert salt is used.

3. PROCEDURE FOR CALCULATING THE OUTER-SPHERE ASSOCIATION CONSTANTS FOR LABILE COMPLEXES

To determine the composition and calculate the outer-sphere association constants for any labile complexes, data from three series of experiments are required[3]. In the first series of experiments complex formation by the central atom M with the ligand L should be studied in the presence of the most inert anions and cations, in the second series of experiments the reaction of the outer-sphere ion with the ligand or with the central ion should be studied, and in the third series of experiments the influence of the outer-sphere ions on the degree of complex formation by the central ion should be studied. The second series of experiments becomes unnecessary if almost no interaction between the outer-sphere ions and the central ion and ligands takes place due to specific features or because of the conditions used.

A procedure has been described[28,33,37] for calculating the association constants for relatively unstable anionic complexes with alkali and alkaline earth metal cations. In this procedure no allowance is made for the interaction of the outer-sphere cations with the ligand, but this simplification is unimportant. When interaction between the outer-sphere ions and the ligand takes place, the calculations by this procedure must be carried out with the equilibrium concentrations of outer-sphere ions B and ligands L. The values of [B] and [L] can be determined experimentally[3] or calculated using the formation constants of BL_n or $B(H_2O)_xL$.

The procedure for calculating outer-sphere association constants given in papers by Mironov and others[3,28,33,37,39] is suitable for calculating the constants for the association of anionic complexes with outer-sphere cations and of cationic complexes with outer-sphere anions. The chief assumption of this procedure is that the activity coefficients of the reacting ions and resulting complexes remain constant in all experiments whose results are used in the calculations.

Complex formation in the absence of outer-sphere association, that is in a medium of the most inert anions and cations, is represented in simplest form by the equilibrium

$$M + nL \rightleftarrows ML_n \qquad (3)$$

and is characterised by the stability constants of the ions ML_n:

$$\beta_n = [ML_n] \cdot [M]^{-1} \cdot [L]^{-n}, \qquad (4)$$

where $n = 1, 2, \ldots N$, and N is the maximum coordination number of M with respect to L under the conditions of the experiment.

† Calculated on the assumption that $a_{L^-} = [L^-]$ or $a_{M^{j+}} = [M^{j+}]$.

Outer-sphere association is represented[3] in simple form by the equilibrium

$$yB + ML_n \rightleftarrows B_yML_n \quad (5)$$

and is characterised by the outer-sphere association constants

$$\gamma_{n,y} = [B_yML_n]\cdot[B]^{-y}\cdot[ML_n]^{-1}, \quad (6)$$

where $y = 1, 2, \ldots Y$, and Y is the maximum number of outer-sphere ions attached to ML_n.

When ionic complexes ML_n are formed, the total concentration of the central ion M (C_M) is defined by the equation

$$C_M = \sum_{n=0}^{n=N} [ML_n]. \quad (7)$$

With allowance for outer-sphere complexes, C_M is given[3,30,32,37] by the equation

$$C_M = \sum_{n=0}^{n=N} [ML_n] + \sum_{y=1}^{y=Y}\sum_{n=1}^{n=N} [B_yML_n]. \quad (8)$$

By expressing the concentrations of ionic and outer-sphere complexes in terms of the stability constants and dividing the right-hand and left-hand sides of Eqns. (7) and (8) by the equilibrium concentration of the central ion, we obtain the equations

$$C_M[M]^{-1} = \Phi = 1 + \sum_{n=1}^{n=N} \beta_n [L]^n \quad (9)$$

and

$$C_M[M]^{-1} = \Phi^{total} = 1 + \sum_{n=1}^{n=N} \beta_n [L]^n + \sum_{n=1}^{n=N}\sum_{Y=1}^{y=Y} \beta_n\gamma_{n,y}[B]^y[L]^n, \quad (10)$$

where Φ is the degree of complex formation by M with L to give ML_n, and Φ^{total} the degree of complex formation by M with L and B to give ML_n and B_yML_n.

Subtraction of Eqn. (9) from Eqn. (10) gives

$$\Delta\Phi = \Phi^{total} - \Phi = \sum_{n=1}^{n=N}\sum_{y=1}^{y=Y} \beta_n\gamma_{n,y}[B]^y[L]^n, \quad (11)$$

where $\Delta\Phi$ is the change in the degree of complex formation by M resulting from the outer-sphere association of ML_n with B.

The unknown quantities in Eqn. (11) are the values of y and $\gamma_{n,y}$, for the values of β_n and n are determined by familiar methods[14] from Φ–[L] data by solving Eqn. (9). To find the numerical values of y and $\gamma_{n,y}$, it is sufficient to measure the dependence of $\Delta\Phi$ on the concentration of outer-sphere ions at several ligand concentrations and then to compile and solve a system of several equations of the same type as Eqn. (11).

Outer-sphere association constants in different systems are calculated[3,8,9,30–34,36,37] using particular forms of Eqn. (11). In practice, the most frequently encountered systems are those in which one complex ion ML_N reacts with one outer-sphere ion[9,53] or in which, of two complex ions ML_N and ML_{N-1} present, the first reacts with two outer-sphere ions and the second with one outer-sphere ion[37,38]. When only BML_N is formed, Eqn. (11) acquires the simpler form

$$\Delta\Phi = \gamma_{N,1}[B]\beta_N[L]^N \quad (12)$$

and when BML_N, BML_{N-1}, and B_2ML_N are formed Eqn. (11) becomes

$$\Delta\Phi = \gamma_{N,1}[B]\beta_N[L]^N + \gamma_{N-1,1}\beta_{N-1}[B][L]^{N-1} + \gamma_{N,2}\beta_N[B]^2[L]^N. \quad (13)$$

A complete analysis of the characteristic features and methods of solution for Eqn. (11) has been published[3,39]. In practice up to the present no studies have been made of systems in which the outer-sphere interaction is described by a more complex form of Eqn. (11) than Eqn. (13). The latter is conveniently solved by a graphical method similar to Leden's method[14,54].

The first stage in the solution of Eqn. (13) involves the construction of the graphical dependence of the function F_1 on the concentration of B ions. The function F_1 is defined by the equation

$$F_1 = \Delta\Phi[B]^{-1}[L]^{-N}\beta_N^{-1} = \gamma_{N,1} + \gamma_{N-1,1}\beta_{N-1}\beta_N^{-1}[L]^{-1} + \gamma_{N,2}[B]. \quad (14)$$

Graphical extrapolation is used to find $\lim F_1$ as $[B] \to 0$

$$\lim_{[B]\to 0} F_1 = \gamma_{N,1} + \gamma_{-N1,1}\beta_{N-1}\beta_N^{-1}[L]^{-1}. \quad (15)$$

In a number of systems studied[3]

$$\gamma_{N,1} \gg \gamma_{N-1,1}\beta_{N-1}\beta_N^{-1}[L]^{-1} \quad (16)$$

and in these cases $\lim F_{1[B]\to 0} = \gamma_{N,1}$. If the two terms on the right-hand side of Eqn. (15) are commensurate, it is necessary in the determination of the values of $\gamma_{N,1}$ and $\gamma_{N-1,1}$ to determine F_1 at not less than two ligand concentrations and then to compile and solve a system of two equations of the same type as Eqn. (15). The solution of this system gives the values of $\gamma_{N,1}$ and $\gamma_{N-1,1}$. It is often impossible to measure the values of the function F_1 at several ligand concentrations even in cases where the two terms on the right-hand side of Eqn. (15) are commensurate. This was the situation, for example, in a study of the outer-sphere associated species formed by bromo-complexes of zinc[37,40] or chloro-complexes of lead(II) with heavy alkali metal cations[38,39]. These complexes were also studied in 4 M $Li(ClO_4$, L) solutions but it was necessary to study the outer-sphere association in 4 M (Li, B)L solutions, since the simultaneous presence of K^+, Rb^+, or Cs^+ cations and perchlorate anions in 4 M (Li, B)(ClO_4, L) solutions is impossible due to the low solubility of the perchlorates of the heavy alkali metals. In these cases[3,37–40] the values of F_1 were determined for 3 M and 4 M (Li, B)L solutions. The values of F_1 for 3.1 M and 3.9 M (Li, B)L solutions were found by making use of the linear dependence of F_1 on the ionic strength of the solution[55,56]. Systems of two equations of type (15) were then compiled. One system was compiled from data for 3.0 M and 3.1 M (Li, B)L solutions and the other from data for 3.9 M and 4.0 M (Li, B)L solutions. Solution of these systems gave the values of γ_N and γ_{N-1} for 3.0 M and 4.0 M (Li, B)L solutions. This method of finding γ_N and γ_{N-1} is based on the assumption that the outer-sphere association constants remain constant when the ionic strength of the solutions is changed from 3.0 to 3.1 and from 4.0 to 4.1. Experimental data confirmed that it is possible to make this assumption[3].

After the determination of $\lim F_1$ as $[B] \to 0$, Eqn. (11) is transformed to

$$F_2 = (\Delta\Phi - \lim_{[B]\to 0} F_1)[B]^{-1} = \gamma_{N,2} \quad (17)$$

and the values of $\gamma_{N,2}$ are calculated. In a number of systems studied with this method of calculating $\gamma_{N,2}$ it was found[3] that the values of the function F_2 depend on the

concentration of B; in this case $\lim F_2$ as $[B] \to 0$ was determined and $\gamma_{N,2}$ was calculated in the same way as $\gamma_{N,1}$.

4. THE MOST WIDELY-USED METHODS FOR DETERMINING OUTER-SPHERE ASSOCIATION CONSTANTS

In recent years a large amount of information has been published[8,9,30-34,37-46] on constants for the association of labile anionic complexes with alkali and alkaline earth metal cations. Most of these data were obtained potentiometrically. Measurements are usually made of the e.m.f. of cells of the type

$$M(Hg)\,|\,S_{LiClO_4}\,|\,3 \quad \text{or} \quad 4\ M\ LiClO_4\,|\,S_x\,|\,M(Hg), \tag{18}$$

$$M(Hg)\,|\,S_{LiL}\,|\,3 \quad \text{or} \quad 4\ M\ LiL\,|\,S_y\,|\,M(Hg), \tag{19}$$

where M represents thallium, lead, bismuth, zinc, cadmium, etc., and L represents chloride, bromide, thiocyanate, iodide, nitrate, or other anions. The solutions S_{LiClO_4} consisted of 0.0001–0.05 M perchlorate of the cation M in 3 M or 4 M lithium perchlorate and the solutions S_{LiL} consisted of 0.0001–0.05 M L_j in 3 M or 4 M LiL. The solutions S_x were prepared by mixing the solutions S_{LiClO_4} and S_{LiL}, and the solutions S_y by mixing the solutions S_{LiL} and S_{BL}. The latter contained 0.0001–0.05 M L_j in 3 M or 4 M BL solution. To suppress the hydrolysis of M, all the solutions studied had a constant acidity, which varied in the range 0.001–1.0 g-ion H^+ litre^{-1}, depending on the stability of the hydroxo-complexes of M.

Other versions of the potentiometric method for determining outer-sphere association constants have been described[3,30] but they are comparatively little used.

Outer-sphere association constants have been determined by polarographic methods[3,30], based on the study of the dependence of the displacements of the half-wave potential of the central M ion on the concentration of L in solutions with compositions analogous to that of solution S_x in cell (18) and also the dependence of these displacements on the concentration of B cations in solutions with compositions analogous to that of solution S_y in cell (19).

The chief disadvantage of these versions of the potentiometric and polarographic methods for studying the interaction in S_x and S_y solutions is that they involve the measurement of the total e.m.f. or displacements of the half-wave potential due to association and diffusion. Thermodynamics does not make it possible to separate the effect of diffusion (the diffusion potential) from the effect of change in the activity coefficients[57]. In practice measurements are made of nominal diffusion potentials, including diffusion and change in the activity coefficients[51].

To increase the accuracy of the potentiometric and polarographic methods for studying association in cells (18) and (19), the diffusion potentials have been determined[3,58] by the flowing junction method[59-61,122].

The solubility of salts of the type ML_j or B_yML_n makes it possible to determine outer-sphere association constants from data obtained by the solubility method[39,62-65].

A large number of papers describe measurements of the solubilities of the halides and thiocyanates of thallium(I)[9,35,66-68], lead(II)[36,39,69], and silver[70], and other sparingly soluble salts with various compositions[40,64,65], usually in solutions with constant ionic strengths. These data have been used to calculate outer-sphere association contants[9,32,36,39,40,53,66,67,70].

Accurate values for the solubility products of sparingly soluble compounds are necessary for calculating the stability constants of ionic complexes and outer-sphere association constants from data obtained by the solubility method[14,16]. In most systems where outer-sphere association constants have been calculated from data obtained by the solubility method, the solubility products were determined potentiometrically[35,36,39,69].

A method has been described[44,45] for calculating the outer-sphere association constants for the anions Br_3^- and $Fe(SCN)_n^{3-n}$, where $n = 4-6$, from the distribution of Br_2 or $H[Fe(SCN)_4]$ between carbon tetrachloride or ethyl ether and 3 M (Li, H, B)L solutions. The extraction method for determining outer-sphere association constants is based on measurement of the distribution constants of Br_2 and Fe^{3+} at different concentrations of the outer-sphere cations[40,44,45].

The spectrophotometric method cannot be used to study relatively unstable outer-sphere complexes, since the latter are ion pairs, whose formation is not accompanied by a significant change in the absorption spectra of the simple ions or ionic complexes[3,40,44,71]. The spectrophotometric and electrical-conductivity methods are the most widely used procedures for studying stable outer-sphere associated species formed by highly-charged, extremely stable, or extremely inert ionic complexes[22].

The spectrophotometric method has been used many times to study the association of cationic complexes with outer-sphere anions, since their interaction is usually accompanied by a change in the spectrum of ML_n.[72-76]

The study of outer-sphere association by an ion-exchange method using cation and anion exchange resins has been described[77].

Data obtained by direct calorimetric measurements[3,40] and the temperature dependence of outer-sphere association constants[9,30,39,41] have been used to calculate enthalpy changes during outer-sphere interaction.

5. OUTER-SPHERE ASSOCIATION AND THE LAW OF MASS ACTION

The change in the stability constants of ionic complexes on going from one salt medium to another is attributed[14,16] to the change in the activity coefficients of M, L, and ML_n, since

$$\beta_n^0 = \beta_n \cdot f_{ML_n} \cdot f_M^{-1} \cdot f_L^{-n} \tag{20}$$

where β_n^0 represents the stability constants relating to the solution with zero ionic strength, β_n the stability constants relating to the solution with a definite salt medium, and f with different subscripts represents the activity coefficients of the species denoted by the subscripts. This explanation of the influence of the salt medium on complex formation in solutions is purely formal, however, since it neglects the fact that any significant changes in activity coefficients are unavoidably associated with definite chemical processes.

The activity coefficients of ions are influenced little by ions of the same sign but are influenced appreciably by ions of the opposite sign[51]. This is explained by the structure of electrolyte solutions[57], in which each ion is surrounded by an atmosphere of ions of the opposite sign. Any ions with charges of different sign naturally attract one another in accordance with Coulomb's law, to form associated species of different types. The formation of any associated species, usually described in the case of strong

electrolyte solutions by the activity coefficients, can be characterised by the constants of the law of mass action[3], if the type of species formed is known and the influence of side processes is excluded. Izmailov[78] emphasised that "the properties of any electrolyte in non-aqueous and even in aqueous solutions must be described on the basis of a process obeying the law of mass action".

It is often possible to isolate the contribution of a definite association process to the influence of the ionic medium on complex formation in solutions[3,30]. The behaviour of certain systems[79] has been described by some workers in terms of formal values of the activity coefficients and by other workers in terms of the constants of the law of mass action.

Before the publication of papers by Mironov and co-workers[32,33], the influence of the salt medium on the stability constants of relatively unstable ionic complexes was always characterised by the changes in the activity coefficients. Experiments and calculations[3,30,32,39] showed that the values of the outer-sphere association constants, calculated from data on the influence of the salt medium on complex formation in solutions in accordance with the procedure described above and measured by various methods, remain almost constant when the concentration of the reacting components is changed by factors of several hundred. This is confirmed by the data in Table 1.

Various methods (Table 1) have been used to determine outer-sphere association constants in systems which might be expected to show a maximum change in these constants[3], for example as a result of a change in the activity coefficients, as a result of the very low stability of ionic complexes, or as a result of the influence of various side-processes. The errors of the determination of the outer-sphere association constants given in Table 1 amount to not less than ±5–40%.[3] In all the systems studied (with the exception of the Na^+–$PbBr_4^{2-}$ system), change in the concentration of ML_n by a factor of 10–500 changed the values of the constants by not more than 10%. The scatter in the values of the constants found by the potentiometric and polarographic methods and by solubility measurements rarely exceeds ±10%.

The values obtained are independent of the method of determination and the concentrations of the reacting substances only for the constants for the association of ionic complexes with the first ion of the outer-sphere. In calculations of the second and third outer-sphere association constants, change in the concentration of ML_n and, more particularly, change in the method of measuring $\Delta\Phi$ changed $\gamma_{n,y}$ by more than 20–80%.[3]

TABLE 1. Outer-sphere association constants for ML_n in 4 M (Li, B)L solutions at 25°.

Outer-sphere cations	Anionic complexes	Outer-sphere association constants, calculated from data obtained by			References
		potentiometric method	polarographic method	solubility method	
Na^+	$TlCl_2^-$	0.10	—	0.08	32
K^+	$TlCl_2^-$	0.14	0.15	0.15	30,32
Cs^+	$TlCl_2^-$	0.22	—	0.25	3,32
Na^+	$PbCl_4^{2-}$	0.73	0.73	0.52*	3,36
Na^+	$PbBr_4^{2-}$	0.11	0.15	0.16	3,30
Na^+	$CdCl_4^{2-}$	0.50	0.51	—	3,33
Na^+	$Pb(NO_3)_4^{2-}$	0.47	0.51	—	3,8
K^+	$PbCl_4^{2-}$	2.1	1.9	2.0	3,30
K^+	$Tl(SCN)_4^{3-}$	0.70	0.70	0.80	3,63
K^+	$PbBr_4^{2-}$	1.0	—	0.95	3,32

* This figure relates to 3 M (Li, B)Cl solutions.

Different methods for studying complex formation in solutions are sensitive to different extents to changes in the activity coefficients of the reactant and product ions[48], so that for the calculation of outer-sphere association constants [according to Eqn. (11) or modifications of this equation] the degree of complex formation by M with L and the degree of complex formation by M with L and B must be measured by the same method. This rule must be obeyed in the study of the stability of outer-sphere complex ion associated species with $\beta_1 < 100$, since in these systems it is necessary to replace more than 20% of the inert ions by ligands[39]. In the calculation of outer-sphere association constants, use is made of the stability constants of the most extensively coordinated ionic complexes, that is, the constants for ML_N, ML_{N-1}, etc. The value of β_N shows its maximum dependence on the changes in the activity coefficients when the composition of an ionic medium with constant ionic strength is varied[39,69,80]. Thus the values of the stability constants of $PbCl_n^{2-n}$ with $n = 1-3$ remain constant in 3 M solutions of a mixture of lithium perchlorate and chloride, but the stability constant of $PbCl_4^{2-}$ is 52 ± 12 according to solubility data[36] and 11 ± 2 according to potentiometric data[80]. This is due to the fact that the $PbCl_4^{2-}$ ion is formed in 3 M Li(ClO_4, Cl) solutions at a chloride ion concentration greater than 0.6 M, that is, in the range of chloride ion concentrations in which the replacement of ClO_4^- by Cl^- changes the activity coefficient of the doubly-charged lead cation[36]. Thus the stability constant of $PbCl_4^{2-}$ ions, determined for 3 M Li(ClO_4, Cl) solutions, includes both the effect of the interaction of the lead cation with four chloride ions and the change in the activity coefficients. If the effect of change in the latter is not to influence the value of the outer-sphere association constants for $PbCl_4^{2-}$, it must be eliminated by using the values of β_N calculated from data obtained using the same method as in the determination of $\Delta\Phi$.

An interesting feature is that the potentiometric and polarographic methods for determining the stability constants of ionic complexes in 3 M and 4 M Li(ClO_4, L) solutions apparently reflect to equal extents the changes in the activity coefficients resulting from the change in the composition of an ionic medium with constant ionic strength[3].

The values of the second outer-sphere association constants calculated using Eqn. (13) are determined by the slope of the linear plot of F_1 against [B]. The replacement of more than 20% of the lithium cations by the cations of other metals in 3–4 M (Li, B)L solutions may lead to a change in the activity coefficients of the reaction ions[35,39]. Thus the slope of the linear plot of F_1 against [B] and hence $\gamma_{n,2}$ may change with change in the method of measuring $\Delta\Phi$ and with change in the concentration of ML_n.

At high concentrations of B in (Li, B)L solutions, an appreciable quantity of BML_n complexes is formed. The statistical mean charge of ML_n is greater than the charge of BML_n, so that the complex BML_n has a greater tendency to add on an additional ligand ion than the free ML_n ion. It may be assumed[3] that the greater part of the change in the activity coefficients of M, L, and ML_n in 3–4 M (Li, B)L solutions with [B] greater than 0.5–2.0 M is due to the conversion of BML_n into BML_{n+1}. The correctness of this explanation is confirmed by a large quantity of

published data[3] which indicate an increase of n in ML_n with increase in the ability of the outer-sphere ions to undergo association with ionic complexes.

6. SOME RULES OF OUTER-SPHERE ASSOCIATION

In the formulation of the rules of outer-sphere association, only the first association constants are used[3], since the values of $\gamma_{n,y}$ for $y > 1$ are arbitrary[14].

The first constants for the outer-sphere association of anionic complexes with alkali and alkaline earth metal cations depend on the dimensions of the outer-sphere cations, being related to the radii of the latter by the equation

$$\gamma_{n,1} = A(r_B - C) \qquad (21)$$

where A and C are constants whose values change with change in M, L, or the charge of ML_n, and r_B the Goldschmidt radii of the outer-sphere cations (in Å). The correctness of Eqn. (21) and of the postulates of the present section is confirmed by the data in Tables 2–4.

The outer-sphere association constants for most labile, relatively unstable chloro-complexes vary according to Eqn. (21) with $C = 0.78$, which is numerically equal to the crystallographic radius of the Li^+ cation. The association constants of bromo-, nitrato-, thiocyanato-, and certain other types of anionic complexes[3,40] are characterised by Eqn. (21) with values of C in the range 0.7–1.1 (Table 2).

The constants for the outer-sphere association of cyanoferrate(III) and other inert highly stable anionic complexes with alkali and alkaline earth metal cations are given by the equation

$$\log \gamma_{n,1} = Ar_B - C, \qquad (22)$$

although within the limits of error of their determination the constants are also described by Eqn. (21) [40,65] (Table 3).

The constants for the outer-sphere association of anionic complexes of low stability with caesium cations (Table 2) are sometimes found to be greater or less than those calculated from Eqn. (21). High values of $\gamma_{n,1}$ are attributed[34] to the inclusion, in the value of the constant, of the increase in the degree of complex formation by M resulting from the increase of n in $CsML_n$. This is apparently the case for the constants for the outer-sphere association of the $ZnCl_3^-$ ion with the Cs^+ cation (Table 2). In general, the possibility that the effect of inner-sphere interaction is included in the value of the first outer-sphere association constant increases with decrease in the stability of the M–L bonds and with increase in the stability of the B–ML_n bonds[3]. From this, it is to be expected that at very low values of β_n and high values of $\gamma_{n,1}$ the values of the latter will depend on the concentration of ML_n and on the method used to determine the outer-sphere association constants.

Low values of $\gamma_{n,1}$ relative to those calculated from Eqn. (21) are attributed to a significant difference between the total and equilibrium concentrations of ligand when C_L is used in the calculations. In the series of alkali metal cations, the stability of the ion pairs $B(H_2O)_xL$ increases from lithium to caesium[82] for $L = Cl^-$, Br^-, I^-, NO_3^-, SCN^-, etc., with the exception of OH^-, CH_3COO^-, etc.[32] Thus the maximum differences between C_L and [L] in the systems whose characteristics are given in Table 2 might be observed for $B = Cs^+$.

TABLE 2. Outer-sphere association constants for anionic complexes at 25°.

Anionic complexes	Constants for association with the cations of					Method of determination*	Medium	References
	sodium	potassium	rubidium	caesium	ammonium			
$TlCl_2^-$	0.10	0.14	0.20**	0.22	—	E	4 M (Li, B)Cl	32
$PbCl_4^{2-}$	0.73	2.1	2.8	3.4	—	E	ditto	3,38
$PbCl_4^{2-}$	0.72	2.1	2.6	3.1	1.0	E	3 M (Li, B)Cl	38,39
$PbCl_4^{2-}$	0.14	0.23	—	1.0	0.9	E	3 M (Li, H, B)Cl with $[H^+] = 1$	3,39
$BiCl_6^{3-}$	0.55	1.5	2.0	2.5	1.3	E	ditto	31
$ZnCl_4^{2-}$	0.40	>1.0	—	—	—	E	4 M (Li, B)Cl	3
$CdCl_4^{2-}$	0.50	1.35	1.8	2.25	0.80	E	ditto	33
$HgCl_4^{2-}$	0.78	1.5	2.0	—	—	E	0.1 M $B_2[HgCl_4]$	3
$ZnCl_3^-$	0.15	0.52	0.70	1.2	—	E	4 M (Li, B)Cl	3
$SnCl_3^-$	0.10	0.50	—	—	—	E	ditto	3
$PbCl_3^-$	0.12	0.53	0.71	0.88	—	E	»	38,39
$PbCl_3^-$	0.09	0.49	0.62	0.82	—	E	3 M (Li, E)Cl	38,39
$ZnBr_4^{2-}$	0.39	1.4	1.6	1.6	1.2	E	3 M (Li, B)Br	37,41
$ZnBr_4^{2-}$	0.46	1.2	1.5	2.4	1.4	E	4 M (Li, B)Br	37,41
$PbBr_4^{2-}$	0.11	1.0	1.4	1.8	—	E	ditto	3,32
$CdBr_4^{2-}$	0.05	0.15	0.22	0.35	—	E	»	3,31
$Pb(NO_3)_4^{2-}$	0.47	1.4	—	—	—	E	4 M (Li, B)NO_3	8
$Zn(SCN)_4^{2-}$	0.052	0.17	0.23	0.72	0.23	E	4 M (Li, B)SCN	40,46
$Zn(SCN)_3^-$	0.013	0.042	0.057	0.18	0.057	E	ditto	40,46
$Pb(SCN)_3^-$	0.015	0.040	0.058	0.074	—	E	»	3,43
$Tl(SCN)_4^{3-}$	0.30	0.80	—	—	—	S	»	3,53
$Fe(SCN)_4^-$	0.009	0.060	0.090	0.13	0.082	Ex	3 M (Li, B)SCN	40,46
$Fe(SCN)_5^{2-}$	0.036	0.24	0.36	0.50	0.33	Ex	ditto	40,46
$Fe(SCN)_6^{3-}$	0.081	0.55	0.81	1.13	0.74	Ex	»	40,46
$Fe(CN)_6^{3-}$	0.17	0.38	—	0.55	—	S	3 M (Li, B)Cl	40,65
$Fe(CN)_6^{3-}$	0.41	—	—	—	—	S	3 M (Li, B)NO_3	40,65
TlI_4^{3-}	0.05	0.20	—	—	—	S	4 M (Li, B)I***	3
ZnI_4^{2-}	—	0.25	—	—	—	E	ditto	4
ZnI_3^-	—	0.06	—	—	—	E	»	40
Br_3^-	0.02	0.30	—	0.80	—	Ex	3 M (Li, B)Br	45
$ZnBr_3^-$	0.10	0.30	0.40	0.50	0.30	E	4 M (Li, B)Br	37,40
$ZnBr_3^-$	0.14	0.29	0.43	0.86	0.43	E	3 M (Li, B)Br	37,40
Cl^-	0.2	0.4	0.6	0.8	—	****	****	82

* E denotes potentiometric method, S solubility method, and Ex extraction method.

** Calculated from solubility data.

*** Calculations carried out using the stability constants of the TlI_4^{3-} ion found for 4 M $Na(ClO_4, I)$ solutions and not for 4 M $Li(ClO_4, I)$ solutions.

**** The constants relate to a solution with zero ionic strength and were calculated using the Fuoss–Onsager equation[82]. The same method[82] gave for the stability constants of $Na^+(H_2O)_xBr^-$, $K^+(H_2O)_xBr^-$, $Na^+(H_2O)_xI^-$, and $K^+(H_2O)_xI^-$ the values 0.2, 0.4, 0, and 0.3 respectively.

Decrease in the charge and decrease in the dimensions of hydrated anionic complexes leads to a decrease in the outer-sphere association constants (Table 2). In the series of anionic complexes $TlCl_2^-$, $PbCl_4^{2-}$, $BiCl_6^{3-}$, $ZnBr_3^-$, $ZnBr_4^{2-}$, $PbCl_3^-$, and $PbCl_4^{2-}$,[3,40] the outer-sphere association constants change according to the equation

$$\gamma_{n,1} = \gamma \cdot Z^2 \qquad (23)$$

where Z is the charge of the anionic complex, and γ without subscript denotes the outer-sphere association constant for the singly-charged anionic complex. In some systems[44,46] this equation has been used to calculate γ_N

TABLE 3. Stability constants of $B^{z+}[Fe(CN)_6]^{3-}$ complexes at 25°.

B	Medium	Stability constants	Method of determination*	References
K^+	0 **	16.6	El	83
K^+	3 M (Li, K) Cl	0.38	S	40,65
Mg^{2+}	0	610	El	83
Mg^{2+}	3 N (Li, Mg) Cl ***	0.094	S	40,65
Sr^{2+}	0	710	El	83
Sr^{2+}	3 N (Li, Sr) Cl	0.17	S	40,65
Ba^{2+}	0	760	El	83
Ba^{2+}	3 N (Li, Ba)Cl	0.25	S	40,65

* El denotes electrical conductivity method and S solubility method.

** 0 — solutions with zero ionic strength.

*** (Li, Mg)Cl — mixtures of lithium and magnesium chlorides.

and γ_{N-1} from $\lim F_1$ as [B] → 0 [see Eqn. (15)]. For example, this method was used to calculate the constants for the outer-sphere association of $Fe(SCN)_n^{3-n}$ ions (n = = 4–6) with alkali metal and ammonium cations[44] (Table 2).

Eqn. (23) is applicable to outer-sphere association constants relating to the same standard state. This equation is not applicable to the outer-sphere association constants found for $PbCl_4^{2-}$ ions in 3 M (Li, B)Cl solutions or to the outer-sphere association constants found for $BiCl_6^{3-}$ anions in 3 M (Li, H, B)Cl solutions with $[H^+]$ = 1 M (Table 2), since an appreciable proportion of the $BiCl_6^{3-}$ ions in solutions with $[H^+]$ = 1 M are bound in $[HBiCl_6]^{2-}$ complexes, which also associate with alkali metal cations. $TiCl_2^-$ anions undergo almost no association with H^+, so that the constants for the formation of the outer-sphere complexes $BTlCl_2$ are little influenced by the replacement of Li^+ by H^+ in 4 M (Li, B)Cl solutions[3] or by the change from 4 M to 3 M (Li, B)Cl solutions.

In the series of anionic complexes $ZnCl_4^{2-}$, $CdCl_4^{2-}$, $HgCl_4^{2-}$, and $PbCl_4^{2-}$, the constants for association with alkali metal cations (Table 2) are inversely proportional to the crystallographic radii of the central ions[3]. The tendency to undergo hydration increases in the opposite sequence of central ions but the dimensions of the hydrated MCl_4^{2-} anions apparently decreases in the sequence given above.

The nature of the central ion has no influence on the outer-sphere association constants for singly-charged anionic complexes (Table 2). The anionic complexes $ZnCl_3^-$, $PbCl_3^-$, and $SnCl_3^-$ have identical constants for association with Na^+, K^+, and Rb^+ cations. The values of the outer-sphere association constants for the singly-charged $TlCl_2^-$ anions differ from those for MCl_3^- ions. This is due to the difference in the dimensions of the hydrated $TlCl_2^-$ and MCl_3^- anions and possibly to a number of other factors[3].

The outer-sphere association constants for MBr_4^{2-} anions decrease in the sequence Zn, Pb, Cd (Table 2); this distinguishes the dependence of the outer-sphere association constants for bromo-complexes on the nature of the central ion from the analogous dependence for the chloro--complexes MCl_4^{2-}. The high values of the outer-sphere association constants for $B^+ZnBr_n^{2-n}$ have been attributed[40] to the low stability of $ZnBr_n^{2-n}$ and the contribution to the value of $\gamma_{n,1}$ due to the increase of n in $ZnBr_n^{2-n}$. This explanation is not convincing, however[3]. Unfortunately, the outer-sphere association constants for $ZnBr_4^{2-}$ anions were determined only by the potentiometric method[40].

The stability of the outer-sphere associated species formed by anionic complexes ML_n^- and ML_n^{2-} decreases with increase in the dimensions of the ligand (Table 2). For example, the constants for the formation of outer--sphere complexes $BPbL_4$, where B represents Na^+ and K^+ cations and L represents chloride, bromide, and nitrate anions, and also the constants for the formation of complexes $BZnL_3$, where L represents chloride, bromide, and iodide anions, decrease in direct proportion to the crystallographic radii of the ligands[40]. The values of $\gamma_{n,1}$ apparently always decrease in the same sense as the dimensions of the ligand, if the values of the outer-sphere association constants are determined with a sufficient degree of reliability[3].

The outer-sphere association constants of thiocyanato--complexes are very low compared with those for halogeno--complexes (Table 2). It may be suggested[3] that the ion pairs $B^+(H_2O)_x(SCN)^-$ are more stable than the analogous compounds with chloride and bromide anions, so that in the calculation of the outer-sphere association constants for thiocyanato-complexes in 3–4 M (Li, B)SCN solutions it is necessary to make allowance for the difference between the total and equilibrium concentrations of thiocyanate ions, since this difference is much larger than in systems containing halogeno-complexes.

The ionic strength of the solutions has little influence on the outer-sphere association constants in the ionic strength range three to four (Table 2).[3] Change in the ionic strength of the solutions from zero to four leads to an appreciable decrease in outer-sphere association constants[40], as in the case of the constants for inner-sphere interaction[3]. A noteworthy feature (Table 3) is that the decrease in the constants for the outer-sphere association of anionic complexes with alkali metal cations on going from solutions with zero ionic strength to solutions with an ionic strength equal to three is much less than that for the analogous characteristics for alkaline earth metal cations. In solutions with an ionic strength equal to three, the constants for outer-sphere association, for example of cyanoferrate(III) anions with alkali and alkaline earth metal cations, are almost identical, but in solutions with zero ionic strength the constants for the attachment of alkaline earth metal cations are several dozen times greater than the constants for the attachment of alkali metal cations (Table 3).

The decrease in the differences between the constants for the attachment of alkali and alkaline earth metal cations on going from solutions with zero ionic strength to solutions with an ionic strength equal to three is attributed[3] (Table 3) to the increase in the interaction of the alkaline earth metal cations with the ligand anions or anions of the salt medium with increase in the ionic strength of the solution[84]. Alkali metal cations also undergo association with ligands or anions of the salt medium, like the alkaline earth metal cations, but this interaction does not have a significant influence on the outer-sphere association constants, if $[ML_n] \ll [B]$. In solutions with equal ratios $[ML_n]/[B]$ and $[L]/[B]$, the $B(H_2O)_xL$‡ complexes are more

‡ The stability constants of $B^+(H_2O)_xCl^-$ in 3–4 M (Li, B)Cl solutions for B = Na^+, K^+, Rb^+, and Cs^+ are 0.4, 0.8, 1.2, and 1.6 respectively[86] if the change from solutions with I = 0 to solutions with I = 3–4 doubles the stability constants.

stable than the $B(H_2O)_xML_n$ complexes, if the charges of L and ML_n are equal. The correctness of this last statement is confirmed by study of electrical conductivity in 3 *N* solutions of mixtures of cadmium chloride with alkali metal chlorides at equal concentrations of $CdCl_2$ and BCl [3,85] and also by potentiometric studies of the stability of the chloro-complexes of cadmium at C_{Cd} = 0.001–0.01 M and high concentrations (up to 5 M) of alkali metal chlorides [41,87]. Data obtained by the electrical conductivity method indicate that the degree of complex formation by cadmium increases in the sequence caesium chloride–lithium chloride, but potentiometric data indicate that the degree of complex formation by cadmium increases in the sequence lithium chloride–caesium chloride. Thus [32] in solutions with equal concentrations of cadmium and alkali metal chlorides the behaviour of the system is determined by the formation of $B^+(H_2O)_xCl^-$ while in solutions with low cadmium concentrations it is determined by the formation of $B^+(H_2O)_xCdCl_3^-$, since the stability of the complexes of both types increases from lithium to caesium.

The stability of the outer-sphere complexes of ML_n with alkali and alkaline earth metal cations increases in inverse or direct proportion to the dimensions of the latter [3]. For association without breakdown of the hydration sheaths of the alkali and alkaline earth metal cations, the stability of the outer-sphere complexes increases in the sequences lithium–caesium and magnesium–barium, but for interaction with breakdown of the hydration sheaths the stability increases in the opposite sequences. From this, it follows that all the complexes whose stability constants are given in Tables 2 and 3 are formed without complete breakdown of the hydration sheaths of the outer-sphere cations; however, the outer-sphere association constants are linear functions of the crystallographic radii of the outer-sphere ions. Under the conditions studied (3–4 M solutions of inert salts) the radii of the hydrated alkali metal cations are apparently inversely proportional to the crystallographic radii of these cations [3]; this explains why the outer-sphere association constants are given by Eqns. (21) and (22).

The enthalpy and entropy changes accompanying outer-sphere association have been determined [3,9,31,32,40,41,81]. The numerical data in Table 4, collected from various papers, show that the interaction of singly-, doubly-, and triply-charged anionic complexes with alkali and alkaline earth metal cations is accompanied by appreciable enthalpy and entropy changes. The decrease in entropy again indicates interaction without complete breakdown of the hydration sheaths of the alkali metal cations [88].

The outer-sphere interaction of quadruply-, quintuply-, and some triply-charged anions is accompanied by an increase in entropy [24], as is the interaction of singly-, doubly-, and triply-charged anionic complexes with outer-sphere cations with low degree of hydration or high charge (greater than three) [89–91].

Increase in the charge or decrease in the dimensions of the anionic complex or outer-sphere cation leads to a smaller decrease in entropy during outer-sphere association (Table 4). The identical decrease in entropy for the association of $PbCl_4^{2-}$ and $BiCl_6^{3-}$ anions with alkali metal cations is attributed to the high acidity of the solutions§ in

TABLE 4. Entropy change accompanying the formation of BML_n at 25°.

Anionic complexes	Entropy change (e.u.) for association with the cations of				Medium	References
	sodium	potassium	rubidium	caesium		
$TlCl_2^-$	—22	—21	—21	—20	4 M (Li, B)Cl	3,9
$PbCl_4$	—	—4	—4	—4	3 M (Li, B)Cl	39
$BiCl_6^{3-}$	—5.0	—3.2	—3.2	—2.9	3 M (Li, H, B)Cl at $[H^+] = 1$	31
$CdCl_4^{2-}$	—26	—23	—22	—20	4 M (Li, B)Cl	41
$CdBr_4^{2-}$	—	—29	—27	—23	4 M (Li, B)Br	81
$PbBr_4^{2-}$	—17	—17	—15	—14	4 M (Li, B)Br	3,32

which the outer-sphere associated species of the chloro-complexes of bismuth were studied (Table 4). In the presence of hydrogen ions even the doubly-charged $PbCl_4^{2-}$ anions react according to the equation

$$H^+ + PbCl_4^{2-} \rightleftarrows HPbCl_4^- \qquad (25)$$

with equilibrium constant equal to five.[3]

The entropy change accompanying the outer-sphere association of one anionic complex with various alkali metal cations is described by the equation [9,31,39,41]

$$\Delta S = 0.1Q_B + A \qquad (26)$$

where Q_B is the heat of hydration of the alkali metal cations and *A* is a constant. The low accuracy of the determination of the entropy change, however, makes necessary repeated verification of the correctness of this statement [3]. These doubts are also raised by the fact that an equation of type (26) characterises the entropy change in substitution processes but not in addition processes [16].

A direct calorimetric method was recently used to measure the enthalpy changes accompanying the association of alkali and alkaline earth metal cations with cyanoferrate(III) anions [40,65]. This increased the accuracy of the determination of the entropy changes. The accurate data [65] showed that the association of $Fe(CN)_6^{3-}$ ions with sodium, potassium, magnesium, and barium cations in 3 *N* solutions of mixtures of lithium chloride with the chlorides of the metals studied is accompanied by a decrease in entropy by 15–17 e.u., the value of ΔS being apparently independent of the nature of the outer-sphere cation.

Association with a decrease in the number of species by unity is accompanied by an entropy decrease of ~17 e.u. [20,92]. This quantity is almost independent of the nature of the interacting species. This result, together with experimental data [40,65], shows that the association of cyanoferrate(III) ions with alkali and alkaline earth metal cations takes place without breakdown of the hydration sheaths of the interacting ions. Spectrophotometric study [65] confirms this conclusion but indicates breakdown of the hydration sheaths in the association of K^+ with $Fe(CN)_6^{4-}$ in 3 M (Li, K)Cl solutions.

The interaction of anionic complexes with highly charged cations ($Z > 2$), weakly hydrated cations, or cations with a tendency to form covalent bonds is usually accompanied by an increase in entropy and a change in the ultraviolet range of the spectrum of ML_n and B. [22,87,89,90] These facts indicate the formation of direct bonds (without the presence of intervening solvent species along the $B–ML_n$ link) between the anionic complexes and outer-sphere cations of these types.

§ In strongly acidic solutions the $BiCl_6^{3-}$ ion is converted into $HBiCl_6^{2-}$, which reacts to form $B^+(H_2O)_xHBiCl_6^{2-}$ with higher positive values of ΔS than $BiCl_6^{3-}$.

Nitrate, sulphate, phosphate, and similar ions are complex anions which do not dissociate in aqueous solutions. The association of these anions with various cations may involve complex formation or outer-sphere association, depending on the nature of the interacting ions. For example, in 3 N $Li(ClO_4, L)$ solutions, Tl^+ forms only ion pairs $Tl^+(H_2O)_xNO_3^-$ with nitrate ions but gives typical complexes with pyrophosphate anions[15]. An intermediate position is occupied by associated species comprising sulphate and thallium[93]. Highly charged cations and cations with a tendency to form stable hybrid bonds form typical ionic complexes with pyrophosphate and sulphate anions and also with nitrate anions[22]. The clearly-defined stepwise nature of their formation distinguishes inner-sphere complexes from outer-sphere complexes. The rules governing the interaction of undissociated complex anions with cations have been examined repeatedly[5,16].

There is as yet no information about the association of labile and relatively unstable cationic complexes with outer-sphere anions, but the outer-sphere association of inert and stable cationic complexes has been studied by many workers[22]. The outer-sphere complexes of the $Co(NH_3)_6^{3+}$ ion have been studied most completely and most frequently, but the data on the stability constants of these complexes are extremely contradictory[3] and are the subject of discussion[62,74]. The values obtained by various workers for the formation constant of the complex $Co(NH_3)_6^{3+}.Cl^-$ lie in the range 0.2–390.[63] Verification of the values of this constant[3] showed that the results of all earlier work[22,74] are correct and that the values of the constants for the formation of the luteochloride complex depend to a marked extent on the concentration and composition of the salt medium in which the studies are carried out[63]. Change in the composition of the salt medium changes the thermodynamic characteristics of the luteochloride complex by factors of several hundred and even changes their sign. Thus the complexes with composition $Co(NH_3)_6^{3+}.Cl^-$ at 25° are formed with $\gamma_{6,1} = 15.3$, $\Delta H = -5.8$ kcal mole^{-1}, and $\Delta S = -11$ e.u. in 0.1–0.5 M sodium chloride solutions but with $\gamma_{6,1} = 0.49$, $\Delta H = 5.6$ kcal × × mole^{-1}, and $\Delta S = 18$ e.u. in a 1 M solution of a mixture of sodium perchlorate and chloride[62]. This sharp change in the thermodynamic characteristics of the luteochloride complex is attributed to a change in the type of association on going from one salt medium to the other. In 0.1–0.5 M NaCl solutions the association of the $Co(NH_3)_6^{3+}$ and Cl^- ions takes place with the formation of a direct bond between the ionic complex and the outer-sphere ion. This is indicated by the decrease in entropy and by the agreement between the values of the outer-sphere association constant determined by solubility and spectrophotometric methods[3]. In 1 M sodium perchlorate solution the luteo-ion forms $\{[Co(NH_3)_6^{3+}].(ClO_4)_x\}^{3-x}$ complexes which are less stable than the complexes with other anions. The replacement of perchlorate ions by chloride ions in 1 M $NaClO_4$ solution leads to conversion of the luteoperchlorate complexes into luteochloride complexes; this process is accompanied by a bathochromic displacement of the absorption band of the luteo-ion in the ultraviolet range of the spectrum and is characterised by an increase in entropy, like the usual process of complex formation in aqueous solutions[5].

The marked influence of the composition and concentration of the salt medium on the thermodynamic characteristics of the ion pairs formed by cationic complexes makes it difficult to compare these characteristics and to recalculate them for solutions with zero ionic strength. Semi-quantitative comparison of a large amount of published data[22] shows that the $Co(NH_3)_6^{3+}$ ion and apparently the ions $Coen_3^{3+}$, $Copn_3^{3+}$, $Pten_3^{4+}$, $Cuen_2^{2+}$, etc., where en represents ethylenediamine and pn propylenediamine, form outer-sphere complexes with various anions, the stability of these complexes (with composition $ML_n.B$) increasing in the order

$$SCN^-, OH^-, I^-, N_3^-, Br^-, Cl^-, S_2O_3^{2-}, SO_4^{2-}, P_3O_9^{3-}, P_4O_{12}^{4-} \quad (27)$$

Increase in the dimensions of the cationic complex decreases the outer-sphere association constants; for example, the stability of the outer-sphere complexes formed by $Co(NH_3)_6^{3+}$, $Coen_3^{3+}$, and $Copn_3^{3+}$ with chloride, sulphate, and other anions decreases with increase in the molecular weight of the amine in the inner sphere[22].

According to modern theories, the stability of the outer-sphere complexes is determined by the charges and dimensions of the ionic complex and outer-sphere ion[94], but the values of the outer-sphere association constants are influenced by the structure of the ionic complex and also, apparently, by the structure of the outer-sphere ion. The *cis*-isomer of $CoCl_2en_2^+$ forms outer-sphere complexes with chloride and acetate anions in aqueous alcohol solutions but the analogous *trans*-isomer does not[49,95]. This can be attributed to the presence of a dipole moment in the *cis*-isomer and its absence in the *trans*-isomer.

The $Cr(H_2O)_6^{3+}$ ion forms less stable outer-sphere complexes with outer-sphere anions than the $Co(NH_3)_6^{3+}$ ion[22]. This difference has been related[94,96] to the higher positive charge of the $Co(NH_3)_6^{3+}$ ion, which has six protons more than the $Cr(H_2O)_6^{3+}$ ion. Increase in the number of protons in cationic complexes of the type $M(RH_n)_6^{3+}$, where RH_n represents molecules containing protons, increases the positive character of the peripheral charge of these complexes[94].

Most ion pairs of cationic complexes are formed by endothermic reactions involving an appreciable increase in entropy[3] and a change in the charge-transfer spectra[72,97]. Linhard[97] showed that the ultraviolet absorption spectrum of the luteo-ion exhibits a bathochromic shift when halide ions are added to a solution of the luteoperchlorate. The magnitude of the bathochromic shift changes in the same sense as the dimensions of the halide ion[72]. The charge transfer in the process

$$[Co(NH_3)_6]^{3+} + I^- \xrightarrow{h\nu} [Co(NH_3)_6]^{2+}.I^0$$

is responsible for the bathochromic shift in the spectrum of the luteo-ion when iodide ions are added to the solution[97].

The outer-sphere association of cationic complexes whose charge exceeds two usually takes place with breakdown of the hydration sheaths of the interacting ions and is accompanied by the formation of direct bonds between the ionic complexes and outer-sphere ions[3] but the nature of this bond has been little studied.

CN^- ions are joined to central cations via the carbon atom[97]. From this, it may be assumed that interaction takes place via the nitrogen atom in the outer-sphere complexes $B[Fe(CN)_6]$. The structures of outer-sphere complexes of the Prussian Blue type are apparently analogous to those of organo-derivatives of gold cyanide. The same is approximately true of the bonds in thiocyanato super-complexes[3¶].

¶ The term "super-complex compound" is synonymous with the term "outer-sphere complex".

The stability of the bond formed by the first halide anions with the luteo-cation increases with decrease in the atomic weight of the outer-sphere ion, but the stability of the anionic super-complexes $\{[Co(NH_3)_6].Hal_x\}^{-x+3}$, where Hal represents halide anions, changes in the opposite sense. This is indicated by chromatographic studies[77] and by study of the solubility of the luteoperchlorate in aqueous solutions of lithium and sodium chlorides and bromides. The increase in the stability of the anionic super-complexes $\{[Co(NH_3)_6].Hal_x\}^{-x+3}$ with increase in the atomic weight of the outer-sphere ion is attributed[77] to the formation of a covalent bond by $Co(NH_3)_6^{3+}$ with halide ions as a result of the donor properties of the latter. This explanation is confirmed[3] by the fact that the values of the stability constants of the luteohalide outer-sphere complexes, calculated from solubility and spectrophotometric data, are identical.

Outer-sphere association has a significant influence on the kinetics of chemical reactions[93,99-101] since outer-sphere complexes of the ion-pair type are more reactive than the free ionic complexes. It cannot be assumed that this is applicable to all systems[3] but up to the present no systems are known[94] in which outer-sphere interaction leads to a significant decrease in the rate of chemical reactions.

The catalysis of a number of redox processes is based on the formation of outer-sphere complexes[99], the catalytic effect increasing in the same sense as the stability of the outer-sphere complexes.

7. PREDICTION OF THE CONSTANTS FOR THE ASSOCIATION OF ANIONIC COMPLEXES WITH ALKALI METAL CATIONS

The results of studies which have been partly summarised in Table 2 and a number of other papers[3,39,40] show that the dependence of $\gamma_{N,1}$ on r_B, r_M, r_L, and Z^2 is linear for most systems studied. These relationships can be used to predict association constants in systems which have not been studied or have been little studied. Experimental verification has confirmed that such prediction is possible[3]. Some predicted outer-sphere association constants[3,40] are given in Table 5. The verification of the numerical data in this Table is of interest.

The dependence of the e.m.f. of cell (19) on the concentration of Na^+ in S_y solutions is linear for all systems studied[3,39], so that for the calculation of the constant for the outer-sphere association of ML_n with Na^+ it is sufficient to measure the e.m.f. of cell (19) at a single Na^+ concentration in the S_y solution. The constants for the association of ML_n with the other alkali metal cations are then most conveniently determined from the plot of $\gamma_{N,1}$ against r_B or the plot of $\log \gamma_{N,1}$ against r_B, knowing that the value of r_B at which $\gamma_{N,1} = 0$ is determined by the nature of the ligand[3] (see section 6).

8. COMPARISON OF OUTER-SPHERE AND INNER-SPHERE ASSOCIATION CONSTANTS

There is a large amount of published information[22] on the composition and stability constants of acido-complexes, determined without allowance for the association of anionic complexes with outer-sphere cations. As a result of such studies, it was found[35,66,67,102-104] that a given central ion forms, for example, a smaller number of ionic complexes and less stable ionic complexes with the halides of light alkali metals than with the halides of heavy alkali metals. An analogous result was observed in the study of nitrato-,[105] thiocyanato-,[68] and other[3] complexes. On the other hand, in a study of hydroxo-complexes[106] it was found that the degree of complex formation by central ions with hydroxide ions increases in the sequence CsOH–LiOH. Calculations of the composition and stability constants of ML_n from data obtained by different methods showed that the values of n and β_n depend on the method of determination[35] and also led to anomalously low or anomalously high values for stepwise stability constants and to the detection of ionic complexes which in fact do not exist in solution[3]. All this was observed when no allowance was made for outer-sphere interaction[3], but these contradictions disappeared in many systems formed by ionic complexes when allowance was made for the formation of outer-sphere complexes, and the constants for the formation of the latter did not depend on the method of determination or the concentration of the reacting substances[32,39].

The need to make allowance for outer-sphere interactions can be seen by comparing the data in Tables 2 and 6, which show that the constants for the attachment of the N-th ligands to ML_{N-1} are less than the constants for the outer-sphere association of ML_N with alkali metal cations for the chloro-complexes of thallium(I), lead(II), zinc, cadmium, and even bismuth(III).[31]

In the formation of nitrato-complexes of lead(II), only the first nitrate anion is joined to Pb^{2+} by a more stable bond than that joining the K^+ cation to the $Pb(NO_3)_4^{2-}$ anion.

TABLE 5. Predicted[3] values of the stability constants of the ion pairs $B(H_2O)_xML_n$ at 25° in 4 M (Li, B)L solutions.

Anionic complexes	Constants for outer-sphere association with the cations of			
	sodium	potassium	rubidium	caesium
$PtCl_4^{2-}$	0.5	1.2	1.6	1.8
$CuCl_2^-$	0.1	0.2	—	—
$AgCl_2^-$	0.1	0.2	—	—
$AgBr_2^-$	—	0.03	0.06	0.08
$SnCl_4^{2-}$	0.6	1.9	2.6	3.0

TABLE 6. Stability constants of ML_n ions in 4 M $Li(ClO_4$, L) solutions at 25°, calculated from potentiometric data.

M	L	Stepwise stability constants of ML_n with n equal to				References
		1	2	3	4	
Tl^+	Cl^-	0.80	0.14	—	—	35
Pb^{2+}	Cl^-	17	3.1	2.3	0.18	80
Zn^{2+}	Cl^-	2.0	0.50	10	0.01	34
Zn^{2+}	Br^-	1.16	0.13	12.7	0.18	37
Zn^{2+}	I^-	0.34	0.03	18	0.31	40
Cd^{2+}	Cl^-	58	6.9	3.7	0.29	33
Pb^{2+}	NO_3^-	3.0	1.2	0.37	0.19	3

Heavy alkali metal cations are joined by a more stable bond to $PbCl_3^-$ and $ZnCl_3^-$ anions than to the four-coordinated chloro-anions. This explains the fact that when Na, K, Rb, or Cs chlorides are added to a solution containing Pb^{2+}, Zn^{2+}, and, apparently, Cd^{2+} cations, the formation of MCl_3^- ions is followed by the formation of $BMCl_3$ outer-sphere complexes, to which the fourth chloride ion is attached. The alkali metal cations are joined to the MCl_3^- anions via a layer of water molecules, but the fourth chloride ion is joined by a direct bond to the central metal ion[3]. This indicates that the outer-sphere interaction without direct bonding between MCl_3^- and alkali metal cations leads to an increase in the coordination sphere of the central ion or, more accurately, increases the probability of the replacement of water in the inner sphere of $[MCl_3(H_2O)]^-$ by a Cl^- anion.

The data in Tables 2 and 6 show that in many systems which have been studied repeatedly the effect of outer-sphere interaction is much greater than the effect of attachment of the last ligands in ML_N, so that the data on the composition and stability constants obtained for these ionic complexes without allowance for outer-sphere interaction[22] require correction†.

9. COMPLEX FORMATION WITH ALLOWANCE FOR ASSOCIATIVE INTERACTION WITH THE IONS OF THE SALT MEDIUM

The composition of the medium, that is the nature and concentration of the solvent and any ions present in the solution, influences complex-formation equilibria. The salt medium may produce either an increase or a decrease in the degree of complex formation by the central ion[3]. A decrease in the degree of complex formation by M with L often takes place when these components form new structural units[15] with the influencing ions, and an increase in the degree of complex formation is observed when outer-sphere complexes are formed by the ionic complexes with the influencing ions. The decrease in the degree of complex formation by M with L under the influence of ions which form new structural units with M or L has been used many times[14] to study complex formation in solution. The increase in the degree of complex formation under the influence of the ions of the salt medium was first taken into account after a series of studies had been carried out in solutions with high and constant ionic strengths, maintained using inert salts[17], but up to the present the allowance made for this effect has been purely qualitative. It is often considered[107] that secondary reasons for the influence of the ions of the salt medium, involving a change in the activity of the solvent, a change in the activity coefficients of the reactant and product ions, a change in the structure of the solution, etc. exert an influence which cannot be distinguished from chemical interaction in systems with labile and relatively unstable complexes. The contents of the preceding sections of the present review refute this suggestion. At present, however, there is little information on outer-sphere interaction or on the dissociation of the alkali and alkaline earth metal salts whose anions are used as ligands in the study of complex formation in aqueous solutions with high and constant ionic strengths.

† The coordination number of the super-Werner sphere is equal to 12; less frequently it amounts to 6 for octahedral complexes and 4 for tetrahedral complexes. The centres of the edges or faces of the tetrahedra and octahedra are used in super-Werner coordination[123].

The replacement of water by aqueous solutions of inert salts smoothes out the difference in the extents to which the dissociation of strong and weak electrolytes obeys the law of mass action[108], so that the interaction of a central ion with ligands and the ions of a salt medium, like the dissociation of all alkali and alkaline earth metal salts, can be characterised by the constants for the formation of definite complexes[3].

Formulae (1) and (2) characterise the composition of the simple ions and ionic complexes formed in concentrated solutions of inert salts. The replacement of any ions of the salt medium influences the composition and structure of the complexes (1) and (2). Increase in the tendency of the ions of the inert salt to react with the central ion decreases the experimentally measured degree of complex formation with the ligand. Thus in the study of the formation of bromo-complexes of lead in solutions with constant ionic strengths, maintained with sodium perchlorate, nitrate, and chloride, it was found[55] that the degree of complex formation of Pb^{2+} in solutions with equal bromide ion concentrations decreases with change in the ions of the salt medium in the sequence ClO_4^-, NO_3^-, Cl^-. This is attributed to the fact that these anions themselves form complexes with the bivalent lead cation, and complex formation with bromide ions involves the replacement, by bromide ions, of the above anions in the inner sphere of the lead cation. The stabilities of the Pb^{2+} complexes increase in the sequence $Pb(ClO_4)_n^{2-n}$, $Pb(NO_3)_n^{2-n}$, $PbCl_n^{2-n}$.[56]

The Li^+ cation forms the least stable outer-sphere complexes with the great majority of anionic complexes with charges less than three[3]. Perchlorate anions rarely form anionic complexes with central ions[22,109] and, more particularly, do not form anionic complexes with charges exceeding three. Thus the stability of complexes of type (1) will be smaller in the presence of Li^+ than in the presence of other cations which do not form stable compounds with the ligand. This explains why, in the interaction of central ions with alkali and alkaline earth metal salts, the highest degree of complex formation by the central ion is observed in a medium containing of lithium salts[110]. This result is not affected by the increase in the stability of the outer-sphere complexes B_yML_n in the sequence lithium–caesium and magnesium–barium[3], since the relative increase in the degree of complex formation by M as a result of the outer-sphere interaction increases with decrease in the stability of the M–L or $M–ClO_4^-$ bonds[103,117].

The stability of the ion pairs $B(H_2O)_xL$, the outer-sphere complexes B_yML_n, and the complexes

$$\sum_{n=0}^{n=N}\sum_{x=0}^{x=X}\sum_{y=0}^{y=Y}\sum_{z=0}^{z=Z} ML_n(H_2O)_xA_yB_z, \qquad (28)$$

by which we mean[14,15,17,54] ionic complexes ML_n in concentrated solutions of inert salts with cation B and anion A, increases from lithium to caesium and from magnesium to barium for different A and L = Cl^-, Br^-, I^-, NO_3^-, SCN^-, SO_4^{2-}, etc.[35,102,103,111], but changes in the opposite sequence for L = OH^-, CH_3COO^-, etc.[3,106] Usually, the stability of the B–ML_n and $B(H_2O)_x$–L bonds changes in the same sequence of cations B, and increase in the strength of these bonds leads to an increase in the degree to which M is bound in complex (28). The anions A, like the cations B, increase the extent to which M is bound in complex (28) with increase in the stability of the M–A bond[3]. Some published data[55,56] contradict this result, due to the fact that the salt medium

was regarded as an inert solvent for M, L, and ML_n, and not as a component of the equilibrium for the dissociation of complex (28).

The cations of the salt medium have little influence on the stability constants of cationic complexes and neutral molecules[63,102,112] if complexes BL_n are not formed. The influence of alkali and alkaline earth metal cations involves chiefly a change in the structure of the cationic complexes, and hence a change in ΔH and ΔS for formation of the latter[20]. The replacement of alkali metal cations in the sequence lithium, sodium, and potassium[113] displaces the equilibrium

$$CdNO_3^+ + xH_2O \rightleftarrows Cd^{2+}(H_2O)_xNO_3^- \quad (29)$$

to the right, since the tendency of these cations to bring about the dehydration of the Cd^{2+} cation decreases in the above sequence.

The influence of the cations of inert salts on the formation of neutral molecules, for example of the type ML_2, is due to their influence[39,43,46,110] on the equilibria

$$2ML_2 \rightleftarrows ML^+ + ML_3^- \quad (30)$$

and

$$3ML_2 \rightleftarrows 2ML^+ + ML_4^{2-} \quad (31)$$

which are often established in stepwise complex formation[3], but which have unfortunately been little studied as yet.

Increase in the tendency of the cations of the salt medium to form outer-sphere complexes with ML_3^- and ML_4^{2-} anions displaces equilibria (30) and (31) to the right and leads to a decrease in the stability constants of ML_2.[43]

The most direct method for investigating complex formation in solutions is by studying the Raman spectra[17,109]. Data obtained by this method are influenced to the minimum extent by the effect of the medium on complex formation and give information about the concentration of individual ionic complexes and also about the nature of the bonds M–L, B–ML_n, and ML–A.[114]

The intensity of the characteristic bands of the Raman spectra is proportional to the concentration of the complex formed and can be used as the chief parameter for the quantitative representation of processes taking place in solutions[114]. Clear-cut measurement of the intensity of the characteristic bands in Raman spectra is possible, however, only for the ionic complexes predominating in the ML, $ML_2 \ldots ML_n \ldots ML_N$ system[115]. The predominating ions are usually ML and ML_N.

Raman spectra are extremely useful for demonstrating the differences between outer-sphere and inner-sphere complexes[109]. The formation of outer-sphere complexes is not reflected in the Raman spectra[116].

The low sensitivity of present-day apparatus unfortunately makes it impossible to use Raman spectra to study complex formation in solutions with reactant concentrations less than 0.5 M.[3] Increase in the sensitivity of the apparatus by several orders of magnitude may make this method the most suitable for studying various types of complex in solution in any salt medium[17].

Despite the low sensitivity of the method, the use of Raman spectra has proved the existence of inner-sphere nitrato-complexes of Ca^{2+}, Ce^{4+}, Th^{4+}, Cu^{2+}, Ag^+, Zn^{2+}, Hg^{2+}, Al^{3+}, and In^{3+} [117,118] and has completely refuted, for almost all elements of the Periodic System, the suggestion that perchlorato-complexes are inner-sphere complexes[109].

The influence of the salt medium on complex formation in solutions often involves the formation of various types of ionic molecules[78] for which allowance is not made in the interpretation of the experimental data[3]. The low energies of formation of ionic molecules points to the possibility of detecting these complexes by means of the vibrational and rotational spectra.

Unfortunately, there is almost no published information on the use of infrared spectra to study the association of ions and the influence of the salt medium on complex formation.

Water absorbs over a wide range of the infrared spectrum. Only the use of thin-layer (5–10 μm) cells or surface reflectance spectra makes it possible to study association in aqueous solutions by infrared spectroscopy and even then only for a limited number of anions.

The sulphato-,[119] thiocyanato-,[120] and cyano-complexes[121] of various metals in aqueous solutions have been studied by infrared spectroscopy. The separate detection of outer-sphere complex formation, usually attributed to the influence of the nature of the salt medium, and inner-sphere interaction showed[119] that the tendency to form inner-sphere monosulphato-complexes decreases in the sequence $Cd^{2+} \simeq Cu^{2+} > Ni^{2+} > Co^{2+} \simeq Zn^{2+} > Mn^{2+}$. The change from the monosulphato- to the disulphato-complexes decreases the contribution made by outer-sphere complex formation[119].

Mathematical treatment of the experimental infrared spectroscopic data sometimes makes it possible to estimate the constants for both inner-sphere and outer-sphere interaction[120].

Increase in the sensitivity and the more extensive use of physical methods for studying association in aqueous solutions should extend our knowledge in this field.

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ELECTRONIC ABSORPTION AND LUMINESCENCE SPECTRA OF AROMATIC POLYCYCLIC HYDROCARBONS

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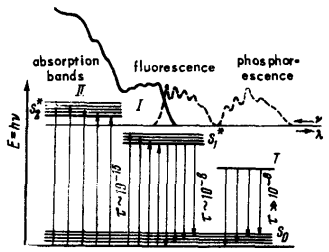
1. ELECTRONIC STATES AND VIBRONIC SPECTRA OF POLYATOMIC MOLECULES

The complete electronic spectrum of a molecule arises from changes in electronic, vibrational, and rotational energy[1-7]. The energy of rotational quanta in polyatomic



molecules is relatively small (the wave numbers corresponding to rotational quanta, which are proportional to their energy, are of the order of $\bar{\nu}_{rot} \simeq 1$ cm^{-1}), and the shape of an electronic band is largely determined by the superposition of the effect of vibrational sub-levels on that of the electronic transition (see Figure). The electronic states of molecules are classified on the basis of the total spin of the electron[1-3,5,6]. As in the case of atoms, a state in which the spins are compensated is called a singlet (S), a state with unit spin is called a triplet (T), and so on. Optical transitions between electronic states in a molecule are controlled by selection rules, according to which transitions between states of the same multiplicity are permitted and transitions between states of different multiplicity are forbidden. Molecular states are further classified on the basis of considerations of the symmetry of the potential field surrounding the nuclear skeleton of the molecule. The symmetry of the wave functions describing particular states of the molecule may not coincide with the symmetry of the skeleton.

In symmetry operations the electronic and the vibrational wave functions undergo similar transformations: hence, classification of these functions and of the states which they describe is possible. We should note that symmetry descriptions are the only precise statements which can be made regarding the wave functions of molecules, since it is impossible, in practice, to obtain the wave functions describing a molecular state in an explicit form. The most convenient classification of states from the point of view of their symmetry is achieved by applying the theory of point groups[1-4,6-9]. Every molecule can be assigned to a definite symmetry group by considering the characteristic symmetry elements of the molecule and symmetry operations. The properties of the transformations of the wave functions stem directly from the concepts of groups. They can be obtained for all groups with which known molecules can be identified. A definite energy state of a molecule with fixed symmetry is called an energy level. The classification of electronic and vibrational states allows us to establish selection rules for optical electronic transitions between energy levels. The probability of a dipolar transition between two states is given by the square of the integral

$$\int \psi^* \hat{\mathbf{M}} \psi^0 \, dv, \qquad (1)$$

where ψ^* is the wave function of the state to which the transition occurs, ψ^0 is the wave function of the initial state, $\hat{\mathbf{M}}$ is the operator of the dipole moment of the transition.

The integral (1) will be non-vanishing if the function within the integral sign (or one of its terms, if the function is in the form of a sum) is fully symmetrical, i.e. if its symmetry properties are identical to those of the molecular skeleton. The function within the integral sign can be fully symmetrical if the product of the terms of the functions under the integral sign ($\psi^* \hat{\mathbf{M}} \psi^0$) gives a fully symmetrical term.

According to the Jahn-Teller theorem[1,2,7], the ground state of a non-linear polyatomic molecule must be non-degenerate and, therefore, fully symmetrical. Hence, a fully symmetrical term will be obtained for the integrand of (1) if the state to which the molecule undergoes a transition from its ground state belongs to the same symmetry type as one of the components of the vector $\mathbf{M}$ (M_x, M_y, M_z in a Cartesian system of coordinates). The selection rules for vibrational-electronic transitions are obtained from formula (1) by putting the wave functions in the form $\psi = \psi_{el}\psi_{vibr}$ (assuming that the rotational state remains unchanged):

$$\int \psi^*_{el} \, \psi^*_{vibr} \, \hat{\mathbf{M}} (\psi^0_{el} \, \psi^0_{vibr}) \, dv. \qquad (2)$$

A purely electronic transition takes place without change in the vibrational state, i.e. $\psi^0_{vibr} = \psi^*_{vibr}$. Multiplication of the vibrational term by itself gives a fully symmetrical term. Therefore, the electronic transition will be allowed if the symmetry of the term ψ^*_{el} coincides with that of one of the components of $\mathbf{M}$ (and the transition will be polarised along the corresponding axis). When an electronic transition is allowed on symmetry grounds, transitions to vibrational sublevels with fully symmetrical terms are also allowed. Vibrations can be active also if they alter the symmetry of the state in such a way that the symmetry of the function $\psi^*_{el}\psi^*_{vibr}$ coincides with the symmetry of one of the other two components of the vector $\mathbf{M}$, the polarisation of the transition changing at the same time by 90°.

If an electronic transition is forbidden on symmetry grounds (so that the purely electronic band is weak, or altogether absent from the spectrum), a vibration of a given symmetry may cause it to become allowed. This requires that the product of the electronic and the vibrational term should belong to the system which describes the transformation of one of the components of $\mathbf{M}$, i.e. should coincide with the symmetry of one of these components. It is evident from formula (2) that strong progressions can occur only with fully symmetrical vibrations, because they do not alter the term in the function within the integral sign even in the overtones. Consider as an example the symmetry group D_{2h}, to which many of the molecules discussed in this review belong. The group D_{2h} includes seven symmetry elements [three mutually perpendicular planes $\sigma(x, y)$, $\sigma(x, z)$, and $\sigma(y, z)$, three second-order symmetry axes c_2^z, c_2^y, c_2^x, and a centre of symmetry], three of which can be independent. Accordingly, eight different types of symmetry are possible, i.e. as many as the number of possible combinations of the signs + and - taken three at a time. Table 1 shows the behaviour of the possible terms of the molecule with respect to symmetry operations.

In the last column of Table 1 the translations T_x, T_y, T_z and the rotations R_x, R_y, R_z are assigned to the symmetry types of pseudo-vibrations. The components of the dipole moment operator $\hat{\mathbf{M}}$ coincide with the components of the vector $\mathbf{T}$. Table 1 shows that the following transitions are allowed for molecules of D_{2h} symmetry: transitions to the state B_{1u} (polarisation along the z axis), to B_{2u} (along the y axis), and to B_{3u} (along the x axis). The products of the various terms can be found from Table 2, which lists the products for the symmetry group.

According to Table 2, in an allowed electronic transition such as A_{1g}–B_{3u} (with polarisation along the x axis)

TABLE 1.

D_{2h}	σ_{xy}	σ_{xz}	σ_{yz}	i	c_2^z	c_2^y	c_2^x	
A_g	+	+	+	+	+	+	+	
A_u	−	−	−	−	+	+	+	
B_{1g}	+	−	−	+	+	−	−	R_z
B_{1u}	−	+	−	−	+	−	−	T_z
B_{2g}	−	+	−	+	−	+	−	R_y
B_{2u}	+	−	+	−	−	+	−	T_y
B_{3g}	−	−	+	+	−	−	+	R_x
B_{3u}	+	+	−	−	−	−	+	T_x

TABLE 2*.

A_{1g}	A_{1u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}	
A_{1g}	A_{1u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}	A_{1g}
	A_{1g}	B_{1u}	B_{1g}	B_{2u}	B_{2g}	B_{3u}	B_{3g}	A_{1u}
		A_{1g}	A_{1u}	B_{3g}	B_{3u}	B_{2g}	B_{2u}	B_{1g}
			A_{1g}	B_{3u}	B_{3g}	B_{2u}	B_{2g}	B_{1u}
				A_{1g}	A_{1u}	B_{1g}	B_{1u}	B_{2g}
					A_{1g}	B_{1u}	B_{1g}	B_{2u}
						A_{1g}	A_{1u}	B_{3g}
							A_{1g}	B_{3u}

* Taken from Sponer and Teller[7].

we may find, in addition to fully symmetrical vibrations, vibrations of B_{1g} and B_{2g} symmetry, which can alter the polarisation of the band: $B_{3u}B_{1g} = B_{2u}$ (along the y axis) and $B_{3u}B_{2g} = B_{1u}$ (along the z axis).

Sponer and Teller have analysed the electronic–vibrational spectra of many polyatomic molecules on the basis of their symmetry properties, and have tabulated the characteristics and products of various symmetry point groups[7].

Lastly, another important effect of the motion and position of the nuclei on the optical transitions in a molecule is expressed by the Franck–Condon principle: neither the relative position nor the velocity of the nuclei can change appreciably during the transition of a molecule from one electronic state to another, because the transition takes place in a time (10^{-15} s) which is short compared to the vibration period of molecules (10^{-12} s). One consequence of this principle is that molecules can undergo only vertical transitions in the potential energy diagram of the electronic states. Since the molecule spends most of the time at the extreme points (of its vibrations), vertical transitions between points on the potential energy curves are the most probable. If the equilibrium distance r is the same for the ground state and the excited state, bands similar to the purely electronic band will show up most strongly in the spectrum. When r changes appreciably, the purely electronic band becomes weak, even for an allowed transition.

It follows from the Franck–Condon principle, which was formulated in terms of classical physics by simultaneously considering the configurations and velocities of the nuclei, that only fully symmetrical vibrations can be active in electronic–vibrational spectra. Tavger's quantum-mechanical analysis of the Franck–Condon principle[10] has led to the conclusion that active frequencies may include some vibrations which are not fully symmetrical. Obviously the number of active, not fully symmetrical, vibrations must be limited by the selection rules according to the symmetry and structural peculiarities of the molecules.

Absorption and Emission Spectra

Under normal conditions (at room temperature) practically all the molecules remain in the electronic ground state of minimum electron energy. The Boltzmann factor kT is of the order of 200 cm^{-1} for T = 20°C (293°K). Therefore, most of the molecules reside in the zeroth vibrational sublevel of the ground state. For the overwhelming majority of known molecules the ground state is a singlet (S_0). As a consequence of the selection rule, S_i–S_k (i.e. singlet–singlet) transitions have the highest probability. Experiment shows that an excited molecule can remain in the lowest excited S_1^* state for a time $\tau \simeq 10^{-8}$ s, and for even shorter times in higher electronic levels. Hence, no appreciable concentration of molecules in excited states will arise during absorption of light by a system of molecules, and under normal conditions transitions of the type $S_{i>0} \rightarrow S_k^*$ will not occur during absorption, but only transitions from the ground state to excited states: $S_0 \rightarrow S_i^*$. The vibrational structure of an absorption band will be determined mainly by the vibrational sublevels of the excited state (see Figure).

A metastable triplet state may arise in the molecule as a result of non-optical and, to a certain extent, of optical transitions (details of the T-state in the molecule are given below). If a molecule is previously excited to a T-level, it is possible to measure absorption bands for $T \rightarrow T_i^*$ transitions (see Karyakin and Duzhenkov's review[11]). The weak bands of forbidden $S_0 \rightarrow T$ transitions are very much harder to observe.

The frequencies of normal vibrations depend on the electronic state of the molecule. Therefore, the vibrational differences obtained from absorption spectra can be expected to differ from the values for the same vibrations as observed in the vibrational spectra.

The lifetime of a molecule in the excited state and its ability to radiate the excitation energy depend essentially on radiationless deactivation processes. These are strongly dependent on the medium, the temperature, the structure of the molecule, and other factors. Light emission by a molecule is possible if the molecule resides in the excited state for a time $\geqslant 10^{-10}$ s. Experiment shows that a molecule can remain for this length of time only in the lowest S_1^* excited state and in its zeroth (vibrationless) vibrational level. Higher excited S_1^* states and vibrational sublevels undergo radiationless deactivation in shorter time intervals, and light emission from the molecule occurs only from the lowest excited S_1^* state (mainly from a vibrationless level) and from a T-state. Radiation caused by an S_1^*–S_0 transition is termed fluorescence. The structure of the fluorescence spectrum is determined by the active vibrations of the molecules in the ground state; therefore, the frequency values should be close to the frequencies of the same vibrations active in the Raman and infrared absorption spectra. The first, purely electronic fluorescence band, if present, should adjoin the long-wavelength edge of the absorption spectrum (partly overlapping the longest-wavelength absorption band), and the whole of the emission spectrum is located in a longer-wavelength region of the spectrum than the corresponding absorption (Stokes displacement of the emission bands, p. 470). The fluorescence yield is not directly related to the intensity of the long wavelength and other absorption bands. When the radiationless transitions are very weak the excited molecule can remain in a metastable T-state for a longer time (more than 10^{-8} s). The triplet nature

of the metastable state was first pointed out by Terenin[5,12], and subsequently by Lewis[13]. It can be demonstrated experimentally by measuring the magnetic susceptibility of the metastable state of a number of molecules[14,15]; more recently it has been demonstrated by electron spin resonance measurements on molecules of aromatic polycyclic hydrocarbons, and some others[16-18].

Under favourable conditions it is possible to observe an emission band due to a $T \rightarrow S_0$ transition accompanied by radiation and known as phosphorescence. The phosphorescence time can amount to several seconds, since the $T \rightarrow S_0$ transition is forbidden by the selection rule. The transition becomes allowed as a result of spin–orbital interaction. Emission spectra can be observed with opaque, scattering specimens, and, what is even more important, at very low concentrations (in some cases as low as 10^{-12} M). Emission spectra have one limitation: not all molecules can luminesce. An important problem in the field of molecular emission spectroscopy is to identify the conditions which favour the appearance of luminescence. It has been found that with many compounds radiationless deactivation is minimised by working with a solid phase and at low temperatures, thus enhancing the luminescence of the molecules.

Influence of the Medium on the Spectra. Quasi-Linear Structure

In practice one observes the spectra not of a single isolated molecule but of a large assembly of molecules, subjected to various external influences. The spectra of vapours may be thought to be those most closely resembling the spectrum of an individual molecule. However, the spectra of polyatomic molecules are usually diffuse owing to the high temperatures involved (which enhance intramolecular interactions, leading to diffuseness of the bands). Without considering in detail the causes of diffuseness in the spectra of vapours, we shall only point out an obvious cause of "diffuseness" in a vibrational sublevel: the quasi-continuous system of rotational sublevels. This, together with other factors, gives a gaseous system of molecules a spectrum whose structure cannot be properly resolved even with a high-resolution instrument. It should be noted, also, that many compounds are not stable in the vapour state. It is easy to see, therefore, why so few data have been published on well resolved absorption and luminescence spectra of complex molecular vapours, especially of polycyclic aromatic hydrocarbons.

Studies of the spectra of aromatic compounds in a condensed phase are more numerous: liquid and solid solutions, pure and mixed crystals. Under these conditions the spectra are significantly affected by intermolecular interactions, which also cause some diffuseness in the structure of the spectra. The most satisfactory resolution of spectral structure in a condensed phase is obtained at low temperatures for pure or mixed crystals and in neutral, very dilute crystalline solutions. In the latter case we are dealing, figuratively speaking, with a "frozen gas". The spectra of these solutions are either indistinguishable from or slightly shifted towards long wavelengths as compared with vapour spectra. In a condensed phase the molecules are closely spaced, and this hinders or altogether prevents molecular rotations. The earliest studies of quasi-linear electronic–vibrational spectra in crystals are due to Obreimov and Prikhot'ko[19,20]. Spectroscopic studies of pure or mixed single crystals having a crystal lattice of known structure, using polarised light, allow the direction of the moments of electronic transitions to be determined with respect to the axes of the molecule. For aromatic hydrocarbons, investigations of this type have been made by McClure (naphthalene in durene[21], phenanthrene[22]), Sidman (anthracene[23], anthracene in naphthalene and phenanthrene[24], naphthacene in naphthalene[25]), Pesteil and coworkers (see review article[26]), and others.

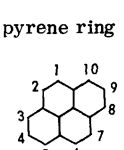
The observation of emission spectra of many aromatic hydrocarbon crystals showing a structure is limited by the photodimerisation effect, involving an excited and a non-excited molecule (excimer formation): the molecular emission band, with a structure, is converted into a structureless emission band at a longer wavelength. This phenomenon has been discussed in detail, for example, in a paper by Stevens[27], but the nature of the phenomenon was made clear by the work of Förster and coworkers[28-31], who studied it in concentrated solutions. Excimer formation from aromatic hydrocarbon molecules in solutions at concentrations above 10^{-3} M suggests the presence of strong interactions involving fluorescing molecules. Therefore, only the spectra of dilute solutions are similar to the spectra of undisturbed molecules. Polarisation measurements on the spectra, enabling the relative polarisation of the various electronic transitions to be determined, are also possible in the case of solutions.

In a series of investigations[32-38], Zimmerman and Yoop have examined the polarisation of the absorption and fluorescence spectra of alcoholic solutions of benzene, naphthalene, anthracene, naphthacene, phenanthrene, 1,2-benzanthracene, chrysene, pyrene, perylene, triphenylene, coronene, and azulene at -180°C. In every case they were able to show that the singlet–singlet bands are polarised in the plane of the molecule. Dörr and coworkers[39-41] showed that the moment of the T–S_0 transition for a series of aromatic hydrocarbons is polarised along a direction normal to the plane of the molecule.

There is no general method for obtaining spectra with an optimum degree of resolution of the vibrational structure, and the problem has to be approached empirically for each individual compound. Shpol'skii and coworkers made an important contribution in this field when they obtained, in 1952, quasi-linear fluorescence spectra for coronene and 3,4-benzopyrene† [42] in crystalline solutions at 77°K. They observed a splitting of the bands into multiplets which has since become known as the Shpol'skii effect. We shall not dwell on the specific features and on the nature of band multiplicity: interested readers are referred to existing review articles[43].

The n-hydrocarbon class of inert solvents has been very useful for resolving the structure of the spectra of many compounds: the study of spectral structure in n-hydrocarbons at low temperatures (77°, 20°, and 4°K) is called the Shpol'skii method. Shpol'skii and his school studied the quasi-linear spectra of many aromatic hydrocarbons[44-66]; their results are used in the present review. In a series of papers[67-69] Sponer, Kanda, and their coworkers showed

† The numbering of the pyrene ring system used by the author is evidently



which is contrary to that adopted by IUPAC and the Chemical Society (Ed. of Translation).

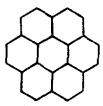
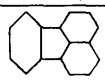
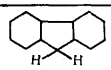
TABLE 3. Frequencies (cm^{-1}) of the electronic $S_1^*-S_0$ and $T-S_0$ transitions of aromatic hydrocarbons.

Formula	$\nu_{S_1^*-S_0}$ and medium	References	ν_{T-S_0} and medium	References	$\nu_{S_1^*-T}$	
(I)	37 800 fl. and abs., hex.	90	29 500 cycl.	67	8300	
(II)	31 730 fl. and abs., pent.	51	21 300 PE	102	10430	
(III)	26 240 fl., hept.	52	14 930 EPA	107	11310	5490/6370
(IV)	21 160 fl., non.	51	10500	80	10660	5080/4430
(V)			8000	80		
(VI)	14 430 abs.					
(VII)	28 820 fl., pent.	71	21 770 hex. 21 800 pent. 21 640	71 78	7020	
(VIII)	26 000 abs. and fl., alc.	35	16 520 16 700	78	9300	
(IX)						
(X)	27 800 fl., oct. 27 900 fl., alc.	64 35	20 000 oct. 19 800 alc. 20 040	64 40 78	7800 8100	
(XI)	25 300 25 440 abs. and fl., pent.	53	18 300 18 260		7000	
(XII)	22 850 abs. 23 000 fl.	73 117				
(XIII)	26 870	73	20 020 20 200	78 119	6670	
(XIV)	25 310 25 350	73 117	18 500 17 900	78	7450	
(XV)	23 120	73				
(XVI)			20 550 alc.	174		
(XVII)			20 080	44 45		
(XVIII)	26 840 fl. and abs., hex. 26 850 fl.	55 36	16 900 hex. 16 850		9940	
(XIX)	26 570 fl., hex.	46	18 630 hex. 18 510	46	7940	
(XX)	24 850 fl., hept.	47	14 670	119	10180	

TABLE 3 (contd.)

Formula	$\nu_{S_1^*-S_0}$ and medium	References	ν_{T-S_0} and medium	References	$\nu_{S_1^*-T}$
(XXI)	25 250 fl., oct.	56	17 000		8250
(XXII)	25 065 fl., oct.	59 60	16 450	59 60	8615
(XXIII)			14 570	119	
(XXIV)			14 050	119	9000
(XXV)	23 920 fl. and abs., hex.	60	16 915	60	7005
(XXVI)	22 460 fl., hex.	49 56	12 040	119	10420
(XXVII)	23 250		11 850	119	11400
(XXVIII)	22 450 fl. and abs., hex. 22 700 fl. and abs., alc.	62 36	12 600	80	10000
(XXIX)	18 860 abs.				
(XXX)	15 090 abs.				
(XXXI)	19 450 abs.				
(XXXII)	17 920 abs.				
(XXXIII)	18 310 abs.				
(XXXIV)	24 625 fl. and abs., hex.	58	16 250 hex. 16 180	58	8375
(XXXV)	15 740 abs.				
(XXXVI)	29 100 fl. 29 140 fl., hex.	120	23 800 23 590 hex. 23 250	120 174	5300 5550

TABLE 3 (contd.)

Formula	$\nu_{S_1^*-S_0}$ and medium	References	ν_{T-S_0} and medium	References	$\nu_{S_1^*-T}$
 (XXXVII)	23 500 fl., hex.	44	19 375 hex. 19 040	50	4125
 (XXXVIII)					
 (XXXIX)	33 160 fl. and abs., hex.	61	23 790 hex.	61	9370

The abbreviations specify the spectra from which the electronic transition frequencies were determined and the solvent used: abs. — absorption spectrum; fl. — fluorescence spectrum; hex. — hexane; PE — petroleum ether; EPA — ether–isopentane–alcohol; oct. — octane; hept. — heptane; pent. — pentane; non. — nonane; cycl. — cyclohexane; alc. — alcohol.

that frozen cyclohexane is a good matrix for resolving the structure of the phosphorescence spectra of various compounds. The present writer has shown, for the case of pyrene in polyisobutylene[62,63], that quasi-linear structure can be obtained also in a polymeric matrix. Bowen and Brocklehurst[70], and also Pesteil and Rabaud[71], have used Shpol'skii's method to obtain quasi-linear spectra for a series of aromatic hydrocarbons.

Among organic compounds which absorb in the visible and near ultraviolet region of the spectrum, aromatic hydrocarbons are the simplest in the sense that their electronic bands in that region are associated with a single type of transition ($\pi-\pi^*$). The problem of establishing the relationship between structure and spectra amounts to formulating the influence of conjugation type (including the geometry of the conjugated system of π-electrons) upon the electronic bands. Polycyclic, fused hydrocarbons have a rigid planar structure which favours the appearance of a vibrational band substructure. The vibrational structure of bands of this class of compounds arises primarily from fully symmetrical vibrations of the carbon skeleton of the molecule (ν_{C-C}). In these cases we can apply a classification in terms of the symmetry of the energy states and establish selection rules for the particular molecule. Practically all known hydrocarbons exhibit fluorescence, and many also phosphorescence (under certain conditions). There is published information both on the absorption and on the luminescence spectra of this class of compounds. Inspection of the relation between the spectra and the structure of the molecules has shown a tendency for the absorption and fluorescence bands in aromatic hydrocarbons to be shifted towards longer wavelengths as the number of benzene rings and of conjugated double bonds in the skeleton of the molecule increases. When the arrangement of benzene nuclei is non-linear the wavelength displacement rule for the electronic bands becomes more complicated. Clar has described the absorption spectra and classified the absorption bands of aromatic hydrocarbons empirically on the basis of intensity differences, differences in the degree of the bathochromic shift with increase in the size of the π-electron system of the molecule, and differences in band shift on going from vapours to solutions[72-77].

α-Bands have a small extinction coefficient ($\log\epsilon \simeq 2.3-3.3$) and appear at the longest wavelengths for many hydrocarbons. On increasing the length of the linear chain of benzene rings, the α-band is usually obscured by a stronger p-band. p-Bands of average intensity ($\log\epsilon \simeq 3.6-4.1$) move rapidly towards longer wavelengths on increasing the linear condensation of nuclei. β-Bands of high intensity ($\log\epsilon \simeq 4.5-5.2$) undergo shifts similar to those of the α-bands as the number of benzene nuclei is increased.

Clar and Zander[78] have collected and discussed the data on phosphorescence spectra for a series of polycyclic hydrocarbons. They point out that the frequency differences between p-bands and the triplet level (of the order of $10-12\times10^3$ cm^{-1}) are approximately constant; T-level positions are listed in other papers[79,80].

Many theoretical discussions of the electronic states and spectra of aromatic hydrocarbons are available: these rely on concepts of the covalent bond, molecular orbitals, and the free electron model. Platt has proposed a perimetric model of the free electron for *ortho*-fused hydrocarbons; with this model, he has calculated the polarisation energies and classified the electronic transitions of many hydrocarbons[81,82]. Platt's band designations ^1L_b, ^1L_a, ^1B_b, ^1B_a, where the subscripts a and b denote polarisation along a particular axis of the molecule, are adopted in the present article. Platt[83] calculated the molecular orbitals by the simple one-electron LCAO method, and also considered[84] the transitions in *peri*-fused hydrocarbons. Ham and Ruedenberg[85] calculated the electronic states of aromatic hydrocarbons on the basis of antisymmetric products of free-electron molecular orbitals. This led to a slight modification of Platt's band classification: their values are shown in brackets in the present article.

There are also theoretical calculations by Pariser[86] and Moffit[87]. An unusual evaluation of transition energies in aromatic hydrocarbons, based on calculated resonance energies of structures in an excited state, has recently been carried out[88].

Table 3 lists the data on the energy of $S_1^*-S_0$ and $T-S_0$ transitions for a number of hydrocarbons.

2. BENZENE AND POLYACENES

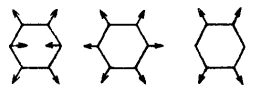
From the point of view of electronic spectra, the polyacene series should be regarded as beginning with naphthalene rather than benzene, because all polyacene molecules (except benzene) belong to the same symmetry group D_{2h}.

The benzene molecule (I)‡ has the D_{6h} symmetry.

In absorption, benzene shows three bands in the region of 2600, 2000, and 1800 Å. The band at 1800 Å ($\log\epsilon \simeq 4.6$) is ascribed to the $A_{1g}-E_{1u}$ transition. The transition is allowed by symmetry and is polarised in the plane of the molecule[89]. The second band at 2000 Å ($\log\epsilon \simeq 3.6$) is resolved into diffuse bands and is associated with the $A_{1g}-B_{1g}$ transition, forbidden by symmetry. The symmetry properties of the B_{1g} state correspond to an alternating distribution of electron density. The symmetry bar

‡ Here and elsewhere in this article, molecules are numbered as in Table 3.

is removed by a vibration of the e_g^+ type. Vibrational series of 160 and 965 cm^{-1} have been identified[89,90]. The weak long-wavelength band of benzene at 2600 Å has been the object of many investigations (see, for example, the review by Jones and Spinner[106]), and has been assigned to the $A_{1g}-B_{2u}$ transition, forbidden by symmetry. In the vapour phase this band is found to split into many narrow bands. A detailed vibrational analysis of this band has been made[7,91], and the vibrations have been assigned to symmetry types It has been shown that the symmetry bar is removed by a vibration of the e_g^+ type, having a frequency of 520 cm^{-1} in the S_1^* state. The fundamental series in the spectrum is determined by fully symmetrical vibrations of frequency 923 cm^{-1}, and begins at the frequency $\nu = \nu_{00} + \nu_{e_g^+} = 38089 + 520$ cm^{-1} (for the vapour). The 923 cm^{-1} vibration corresponds to a "breathing" vibration of the ring



520 + 923 = 1443 (in the S_1^* state); 606 + 992 = 1600 cm^{-1} (in the S_0 state).

The frequency 1600 cm^{-1} is often very active in the spectra of compounds containing benzene rings. The weak fluorescence band of benzene, in the region of 2700–3100 Å, is associated with the same $B_{2u}-A_{1g}$ transition, forbidden by symmetry. In emission the transition becomes allowed as a result of the e_g^+ vibration of frequency 606 cm^{-1}, but the fundamental series is associated with a vibration at 992 cm^{-1}. The structure of the fluorescence spectrum of benzene is well resolved at 77°K in cyclohexane solution. According to Braude[90], in hexane the ν_{00} frequency of the $S_1^*-S_0$ transition is 37800 cm^{-1}. A phosphorescence spectrum with a structure has been obtained[92] in a matrix of cyclohexane at 77°K (and also[67] at 77° and 4.2°K). The $T-S_0$ spectrum has been interpreted by Sponer and coworkers[67] starting with the doublet at 29501/29442 cm^{-1}, referred to the 00 band, with the help of the e_g^+ vibration frequencies 607, 1178, 1590/1607 cm^{-1}, of the b_{2g} vibration frequencies 698, 988, 1458 cm^{-1}, and of the series of fully symmetrical vibrations (frequency 992 cm^{-1}). A vibrational analysis of $T-S_0$ spectra has also been given by Shull[93] and by Dikun and Sveshnikov[94].

The frequency difference $\nu_{S_1^*-T}$ in benzene amounts to 8300 cm^{-1}.

Naphthalene (II). Symmetry D_{2h}. Three electronic bands can be distinguished in the absorption spectrum[73]: ^1L_b (31750), ^1L_a (34500), ^1B_b. The most intense short-wavelength band at 220 nm is practically structureless, and is associated with the $A_{1g}-B_{3u}$ transition, polarised along the long axis of the molecule[21,32]. The broad ^1L_a band in the region of 2900–2300 A, with a weakly developed vibrational structure, is associated with the $A_{1g}-B_{3u}$ transition, polarised along the x axis, as shown by McClure[21] in his study of the absorption spectrum in polarised light of a mixed naphthalene–durene single crystal, and by Zimmerman and Yoop[32] on the basis of polarisation absorption and luminescence spectra of solutions at -180°C. The weakest long-wavelength absorption band (3300–2900 Å) has a sharp vibrational structure in many solutions at low temperatures, and is ascribed to an $A_{1g}-B_{2u}$ transition. McClure[21] separated two series of bands in the vibrational structure: a series of weak bands, beginning from the purely electronic band, polarised along the y axis, and a stronger series of bands, whose origin lies 509 units higher (on the cm^{-1} scale) than the 00 band. The 3300 Å fluorescence band of naphthalene, associated with the same $B_{2u}-A_{1g}$ electronic transition as the long-wavelength absorption, also has a well developed vibrational structure. Bolotnikova[51] has described the quasi-linear structure of the fluorescence band in pentane solution at 77°K. McClure distinguished two systems, having mutually perpendicular polarisations, in the fluorescence spectrum. Similar results were obtained by Bolotnikova in her vibrational analysis of fluorescence in pentane. She identified the most active frequencies (517, 772, 1033, 1386, 1465, and 1579 cm^{-1}) and assigned them to fully symmetrical skeletal vibrations. The 500 cm^{-1} interval by which the origin of the second series is separated from the 00 band (ν_{00} = 31731 cm^{-1}) was assigned to a vibration of b_{1g} symmetry. Papers on the long-wavelength absorption[95] and emission[96-98] bands of naphthalene vapour give a detailed vibrational analysis of the electronic bands. The results for vapour spectra agree with the analysis of solution spectra: two series of bands, with a 506 cm^{-1} difference in relative position, can be distinguished also in the spectra of the vapour. (In the vapour, ν_{00} for the long-wavelength transition is 32017 cm^{-1}). The vibration frequencies obtained from an analysis of the vibronic spectra are in good agreement with the frequencies obtained from the vibrational spectra of naphthalene[99] and also with the theoretically calculated values[100,101].

The phosphorescence spectrum in a propyl ether–isopentane solution at -190°C begins with a strong band ($\nu_{00} \simeq$ $\simeq$ 21300 cm^{-1}) and can be resolved into 20 bands, interpreted[102,103] in terms of the frequencies 512, 1146, 1380, and 1575 cm^{-1}.

Anthracene (III). The absorption spectrum is characterised by three electronic bands with a sharply resolved vibrational structure: ^1L_a (26000), ^1B_b (40400), $^1C_b(^1B_a)$ (45000 cm^{-1}).[73]

Sidman[24] measured the absorption bands in polarised light for anthracene–naphthalene and anthracene–phenanthrene crystals, and showed that the transitions ^1L_a and $^1C_b(^1B_a)$ are polarised along the x axis, whereas the ^1B_b transitions are polarised along the y axis. These results were confirmed[32] by measurements of the absorption and fluorescence polarisation spectra of solutions, and also[104] by measuring the dichroism of the absorption bands in stretched films. Polarisation of a similar type was observed also for pure single crystals of anthracene[23,105]. Jones and Spinner[106] give an analysis of the structure of the absorption bands in pentane solution at -100°.

p-band: $\nu(26570 + 390n_1 + 790n_2 + 1440n_3)$ cm^{-1} ($n_1 =$ $= n_2 = 0,1$; $n_3 = 0-5$).

β-band: $\nu(39460 + 300n_1 + 1070n_2 + 1370n_3)$ cm^{-1} ($n_1 = n_3 = 0,1$).

A detailed analysis of the long-wavelength band, associated with the $A_{1g}-B_{3u}$ transition, was published by Sidman[24] for a mixed crystal at 4°K and by Bolotnikova[52] for a heptane solution at 77°K. The structure is determined mainly by a 1400 cm^{-1} series, assigned to a fully symmetrical vibration.

The blue fluorescence band of anthracene lies almost entirely in the visible region of the spectrum. The best resolution of this structure was obtained[52] in solution at

77°K, when the purely electronic band (26241 cm^{-1}) was separated from the vibrational frequencies (390, 1037, 1165, 1407, 1565, 1645 cm^{-1}), assigned to fully symmetrical vibrations. Sidman[24] gave an analysis of the fluorescence band of anthracene in a mixed crystal. It is interesting to note that the 403 and 1416 cm^{-1} frequencies in the spectrum of the mixed crystal are reduced to 390 and 1407 cm^{-1} in the spectrum of the heptane solution. Intense series in the fluorescence band are associated with the frequency 1407 cm^{-1}.

Zimmerman and Yoop[32] analysed the structure of the band in absorption and in emission on the basis of polarisation spectra of the solution at -180°C. They resolved two series of bands, polarised in mutually perpendicular directions. The main series, with its origin in the 00 band, is polarised along the x axis: $\nu_N = \nu_{00} \pm n_1\nu_1 \pm n_2\nu_2$ (ν_{00} = = 26000 cm^{-1}, $\nu_1 = 1400$, $n_1 = 0, 1, 2$; $\nu_2 = 500$, $n_2 = 0, 1$), and the subsidiary series has $\nu_N = \nu_{00} \pm 900 \pm n_1\nu_1 \pm n_2\nu_2$, polarised along the y axis (the + sign refers to the absorption bands, the - sign to the emission bands). As in the case of naphthalene, the difference of 900 cm^{-1} must be assigned to a vibrational frequency of b_{1g} symmetry. The same authors[32] point out certain minima in the polarisation absorption spectra at 28500 and 30000 cm^{-1}, which they tentatively ascribe to a ^1L_b transition in absorption, since according to theory the weak ^1L_b band should be hidden by the ^1L_a band.

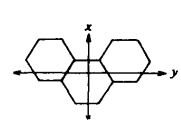
Anthracene has a phosphorescence band in the infrared region. The structure of the T–S_0 spectrum has been described[107] in terms of an initial band at 14928 cm^{-1} and vibrational frequencies of 410, 1137, 1266, 1414, and 1573 cm^{-1}. The transition is interpreted as $^3B_{2u}$–$^1A_{1g}$, and the frequencies are assigned to fully symmetrical vibrations.

Naphthacene (IV). ^1L_b and ^1L_a bands have been identified[73] in the absorption spectrum. According to theory, the weak $^1L_b(\alpha)$ band is concealed by the ^1L_a band. Studies of the polarisation of the spectra of naphthacene in naphthalene have shown[25] that the ^1L_a band is polarised along the short x axis, whereas the ^1L_b and ^1B_b bands are polarised along the y axis. Sidman gives a detailed analysis of the structure of the long-wavelength absorption and fluorescence bands of a mixed crystal. Bolotnikova[52] analysed the vibrational structure of the given fluorescence spectrum of naphthacene in nonane at 77°K, and found a structure identical to that of the fluorescence in naphthalene. She isolated the frequencies at 321, 462, 615, 1165, 1473, and 1380 cm^{-1}. The intense series of the last frequency determines the form of the fluorescence spectrum. The data on the polarisation of the electronic transitions were confirmed by Zimmerman and Yoop[32]. The weak minima at 25000 and 26400 cm^{-1} in the polarisation absorption spectra are ascribed to a ^1L_b transition. The same authors also describe[32] the vibrational structure of the polarisation fluorescence spectrum. The initial band at 20000 cm^{-1} consists of two superimposed bands with mutually perpendicular polarisation, from which two series of bands with a 1400 cm^{-1} period originate. Only a calculated value (~10500 cm^{-1}) of the energy of the T–S_0 transition appears to be known[80]. The quoted value[79] ν_{phos} = 19600 must be ascribed to impurity phosphorescence. Clar and Zander[78] have shown that the phosphorescence bands disappear upon careful purification of naphthacene. It has been suggested[60] that the impurity is naphthacenequinone.

The long-wavelength band of pentacene (V) extends over the whole of the visible region 6000–4000 Å (the T-level[80] is in the region of 8000 cm^{-1}). The last of the polyacenes which have been prepared, hexacene (VI), absorbs[73] in the region 7000–5500 Å ($\nu_{S_1^*-S_0} \simeq 14430$ cm^{-1}). Polyacenes with a larger number of rings are unstable. The long-wavelength absorption band and the fluorescence spectrum of anthracene, naphthacene, and pentacene show a similarity in their vibrational structure, which is determined mainly by a vibrational difference of 1400 cm^{-1}. In the polyacene series (benzene, naphthalene, anthracene, naphthacene, pentacene, and hexacene) the energy of the S_1^*–S_0 and T–S_0 transitions decreases as the number of benzene rings increases by the following amounts respectively: 6300 (8000 for T–S_0), 7000 (6600), 5000 (4000), 4000 (2500), 3000 cm^{-1} (see Table 3). The drop in energy becomes gradually smaller as the number of rings increases. At the same time, the energy difference between the S_1^* and the T states retains its value (10000 cm^{-1}) practically unchanged, with only a slight decrease.

3. ANGULAR *ortho*-FUSED HYDROCARBONS

Phenanthrene, of C_{2v} symmetry, the simplest angular hydrocarbon, is an isomer of anthracene. It was originally suggested that its spectroscopic characteristics should be similar to those of anthracene. In practice, its spectra are much more complicated, and quite different from those of anthracene. The bands of four electronic transitions can be distinguished in the absorption spectrum: ^1L_b, ^1L_a, ^1B_b, and $^1C_b(^1B_b)$. Calculation predicts that the ^1L_b and $^1C_b(^1B_b)$ transitions should be polarised along the x axis, whilst the ^1L_a and $^1B_b(^1B_a)$ transitions are polarised along the y axis. McClure studied the spectrum of the ^1L_b absorption band of a crystal at 20°K in polarised light, and showed[22] that the band of the 00 transition (28660 cm^{-1}) is polarised along the x axis. It follows from measurements of the polarisation absorption spectra in ethanol solution at -180°C that the 00 band of the ^1L_b transition is polarised at right angles to the bands of the ^1L_a (3400 cm^{-1}) and ^1B_b (39300 cm^{-1}) 00 transitions. Zimmerman and Yoop[35] report that weak bands at 34900 and 38200 cm^{-1}, polarised along the x axis, are also present in the spectrum. The ^1L_b band has a clearly defined vibrational structure in the polarisation spectrum, due to the presence of two series of bands polarised in mutually perpendicular directions. The main series begins at the 00 band: ν_N = 28900 cm^{-1} + $+ n_1\nu_1$(ν_1 = 1400 cm^{-1}; n_1 = 0, 1, 2). The origin of the secondary series differs by 700 cm^{-1}: ν_N = 28900 + 700 + $+ n_1\nu_1$. Popov[104] studied the dichroism of absorption bands in stretched films and showed that the ^1L_b transition is polarised along the x axis, whilst the ^1L_a and ^1B_b transitions are polarised along the y axis. He also discovered in the dichroism curve a structure within the ^1L_b band, which he associated with the appearance of a not fully symmetrical vibration at 670 cm^{-1}.



Later workers obtained a better resolution of the vibrational structure of this band, and showed that it arises from the large number of frequencies which are active in the vibrational spectrum. McClure published an analysis

of the structure of the absorption band of crystalline phenanthrene[22]. Kharitonova[108] examined the structure of the absorption bands of the vapour, and distinguished the frequencies ν_{00} = 29 120 cm^{-1} and ν_{vibr} = 680 and 1420 cm^{-1} in the ^1L band. In the second band, with $\nu_{00} \simeq$ 35 200 cm^{-1}, she found ν_{vibr} = 360, 470, 680, 960, and 1400 cm^{-1}.

The fluorescence spectrum, investigated under a variety of conditions, shows a well resolved vibrational structure. The polarisation structure of the fluorescence spectrum[35] indicates the presence of two series of bands, polarised at right angles to each other. The main series begins at the 00 band, and the origin of the second series is separated from it by the frequency of a vibration of b_2 symmetry whose value could not be accurately determined.

Pesteil and Rabaud[71] obtained an extensive quasi-linear structure in the fluorescence band of a pentane solution at 20°K. The spectrum, with a band head at 28 818 cm^{-1}, was interpreted with the help of more than 30 frequencies, some of a_1 symmetry, and some apparently b_2 symmetry. The authors[71] also made a detailed analysis of the phosphorescence spectrum under the same conditions, found in a region of lower frequencies (~7020 cm^{-1}). Kanda and Shimada[109] analysed the T–S_0 spectrum in ether–isopentane–alcohol and in petroleum ether media at 90°K. In solution in polypropyl ether–isopentane the phosphorescence band splits into 16 bands at 77°K: $\nu_{00} \simeq$ 21 730, $\nu_{vibr} \simeq$ 406, 1417, 1608 cm^{-1}. According to Cropper and Dörr[39], the T–S_0 transition is polarised at right angles to the plane of the molecule, and some not fully symmetrical vibrations are active in the T–S_0 spectrum in addition to the fully symmetrical vibrations. As regards phosphorescence, phenanthrene shows some further differences from anthracene. The initial band of its bluish-green phosphorescence lies at even higher frequencies than the green phosphorescence band of naphthalene. These facts suggest that Clar's hypothesis[74], according to which the π-electron cloud of phenanthrene can be regarded as the π-electron cloud of biphenyl plus an ethylene group (for the ground state of the molecule), is not applicable to these spectra. The long-wavelength transitions of biphenyl and phenanthracene are polarised at right angles to each other, but the energy of the transition is higher in biphenyl than in naphthalene, whilst it is lower in phenanthrene. We should note that the spectroscopic characteristics of phenanthrene are, perhaps, closer to those of naphthalene than to those of anthracene. This similarity between the spectra of 1,2-benzopolyacenes and those of the parent polyacenes becomes even more apparent with longer polyacene units.

1,2-Benzanthracene (tetraphene) (VIII). Four absorption systems have been distinguished in the absorption spectrum: ^1L_b, ^1L_a, ^1B_b, and $^1C_b(^1B_a)$. The 00 bands for these transitions in alcohol solution at -180°C occur[47] at 26 000 cm^{-1} for ^1L_b, 27 300 cm^{-1} for ^1L_a, 34 400 cm^{-1} for ^1B_b, and 43 500 cm^{-1} for ^1C_b. Experimental data on the polarisation of the electronic bands are in approximate agreement with theory[100], but they give somewhat different values for the angles between the polarisation vectors[35]. The regions of the different mutually overlapping electronic bands have been identified[110] from the temperature dependence of the spectra. The results[100], given in Table 4, do not agree entirely with the analysis of the bands[35].

Sandorfy and Jones[111] have analysed the absorption spectra in pentane at -100°C in the region 26 000–33 000 cm^{-1}, and have distinguished two series of bands with a spacing of 1400 cm^{-1}.

TABLE 4.

Band region (cm^{-1})	Type (after Zhirnov[100])	Type (after Craig et al.[98])
26 000–31 000	^1L_b	α
27 000–33 000	^1L_a	p
33 000–35 000 (Possibly 37000)	^1B_b	
33 000–38 000	^1B_a	β
	Three other electronic band systems were not interpreted	

The fluorescence spectrum[111,112] of a solution at room temperature consists of wide bands with ν_{00} = 26 000 cm^{-1} and an interband spacing ν_{vibr} = 1400 cm^{-1}. The first phosphorescence band has a frequency about 9500 cm^{-1} lower than the fluorescence band[102,113]. In solution in isopentane–methylcyclohexane (1 : 4) at 77°K the phosphorescence spectrum shows three maxima: at 6060 (15 500 cm^{-1}, 6570, and 7250 Å. In a propyl ether–isopentane solution the phosphorescence band splits into 6 bands in the region of 16 700 (ν_{00})–11 200 cm^{-1}; their frequencies are given by the series $\nu = (\nu_{00} - 400n_1 - 1350n_2)$ cm^{-1}.

The T level in 1,2-benzanthracene is found to be somewhat higher than in anthracene (just as it is higher in phenanthrene than in naphthalene). Angular fusion of a benzene ring in the 1,2-position in polyacenes is accompanied by an increase in the relative height of the T level, or by a decrease in the difference $\nu_{S_1^*-T}$. For the longer polyacenes [1,2-benzonaphthacene (IX), 1,2-benzopentacene], only the absorption spectra are known. The long-wavelength bands are fairly similar in position and vibrational structure to those of the parent polyacenes. We shall now consider angular molecules formed by a centro-symmetrical combination of benzene rings.

Chrysene (X). Symmetry C_{2h}. The absorption spectrum contains four electronic bands: ^1L_b, ^1L_a, ^1B_b, $^1C_b(^1B_a)$.

An analysis of the polarisation absorption and fluorescence spectra gave approximate agreement with theory, with slightly different values of the angles[35]. The following values are reported[35] for the 00 band frequencies: 27 800 cm^{-1} for ^1L_b, 30 900 cm^{-1} for ^1L_a, 37 000 cm^{-1} for ^1B_b, and 44 100 cm^{-1} for $^1C_b(^1B_a)$. Although the chrysene molecule contains four benzene rings, the long-wavelength transition in this molecule has an energy intermediate between those of phenanthrene and anthracene. The vibrational structure of the ^1L_b absorption band has been analysed[64] as for the crystalline state.

The structured band spectrum of the deep blue fluorescence[13,114] in solution in ether-isopentane–alcohol at -190°C begins with a band having $\nu_{00} \simeq$ 27 800 cm^{-1}. The difference ν_{vibr} = 1370 cm^{-1} has been identified[115] in the fluorescence spectrum of the crystals. Nurmukhametov and coworkers[64] have analysed the vibrational structure of the quasi-linear fluorescence spectrum in octane solution at 77°K, and have identified the vibrational frequecies 295, 875, 1180, and 1395 cm^{-1}, the last being the most characteristic of the spectrum. Two series of bands, polarised at right angles to each other, have been detected[35] in the polarisation fluorescence spectra of an alcohol solution at 90°K: $\nu_N = \nu_{00} - n_1\nu_1$ (ν_{00} = 27 900, ν_1 = 1400) cm^{-1}, n_1 = = 0, 1–3; $\nu_N = \nu_{00} = 800 - n_1\nu_1$. Dörr and Cropper[40]

have demonstrated the presence of two subsidiary series with identical polarisation: $\nu_{N'} = \nu_{00} - 300 - n_1\nu_1$ and $\nu_{N''} = \nu_{00} - 800 - n_1\nu_1$ (where $\nu_{00} = 27\,800$, $\nu_1 = 1400$ cm^{-1}, $n_1 = 0,1-4$).

The T level in chrysene is lower than the S_1^* level by 7500 cm^{-1}, i.e. approximately by the same amount as in phenanthrene. The vibrational structure of the phosphorescence band in octane solution has been analysed[35] in terms of the frequencies ν_{vibr} = 300, 646, 1230, 1375, and 1617 cm^{-1} ($\nu_{00} = 20\,000$ cm^{-1}). The phosphorescence in ether–isopentane–alcohol at -190°C has been described. Measurements of the polarisation phosphorescence spectra[40] have shown that the $T-S_0$ transition is polarised at right angles to the plane of the molecule, and in alcohol solution has the frequency $\nu_{00} \simeq 19\,800$ cm^{-1}. The phosphorescence spectrum shows a definite similarity to the phosphorescence spectrum of phenanthrene. The frequencies 300 and 375 must be assigned to not fully symmetrical vibrations, the remainder to fully symmetrical vibrations.

1,2; 5,6-Dibenzanthracene (XI). Symmetry C_{2h}. Clar distinguished three electronic bands in the absorption spectrum of its benzene solution: α (with maxima at 3950, 3850, 3730 Å), p (3510, 3365, 3220 Å), and β (3000, 2900, 2770 Å).

Bolotnikova[53] analysed the vibrational structure of the long-wavelength absorption band in pentane at 77°K, assigned the 25 441 cm^{-1} band to a 00 transition, and identified the differences 488, 605, 691, 748, 1355, 1445, and 1586 cm^{-1}. The fluorescence band of the solution at room temperature consists of three maxima[117] (25 400, 24 000, and 22 500 cm^{-1}); at 77°K the band splits, in hydrocarbon or alcoholic solutions, into 13 bands[118], and in pentane–octance solutions it splits into a large number of bands with initial $\nu_{00} \simeq 25\,442$ cm^{-1}. In the vibrational structure the following differences have been identified: 220, 320, 453, 495, 544, 588, 620, 721, 880, 1153, 1296, 1343, 1590, and 1765 cm^{-1}.

Butlar and Grebenshchikov[120] report the values 25 300 and 18 300 cm^{-1} for the $\nu_{S_1^*-S_0}$ and the ν_{T-S_0} transition frequencies respectively.

It should be noted that the S_1^* level is only 550 cm^{-1} lower, and the T level is actually 1500 cm^{-1} higher, than the corresponding levels in benzanthracene. Therefore, angular fusion of one additional ring leads to even closer approach of the energies of the S_1^* and T levels. The great similarity between the absorption curves of benzanthracene and dibenzanthracene is also noteworthy.

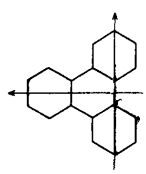
1,2; 7,8-Dibenzonaphthacene (XII). Symmetry C_{2h}. Clar isolated p and β bands, having a coarse vibrational structure at room temperature, in the absorption spectrum of a benzene solution of this compound. The average interval is ν_{vibr} = 1400 cm^{-1} for the p band. The structure of this band is very similar to those of naphthacene, benzonaphthacene, and dibenzonaphthacene. The initial ν_{00} band is quite strong (22 851 cm^{-1}), and has a higher frequency than the corresponding bands in naphthacene and benzonaphthacene. The fluorescence band[117] has three maxima: 23 000, 21 500, and 20 100 cm^{-1}. The T level is located at 18 000 cm^{-1}, i.e. 7300 cm^{-1} below the S_1^* level.

The absorption spectrum of 1,2; 8,9-dibenzopentacene in methylnaphthalene is reminiscent of the spectra of pentacene and benzopentacene, but this spectrum too occurs at shorter wavelengths than those of the last named hydrocarbons. The corresponding seven-ring linear polyacene is quite unstable. Less is known about the spectra of hydrocarbons having two benzene rings fused angularly to the polyacene chain symmetrically with respect to the short axis of the polyacene.

3,4-Benzophenanthrene (XIII) has a very unusual absorption spectrum with a 00 long-wavelength transition band (26 874 cm^{-1}) somewhat lower than in chrysene. The T level[119] is at 20 200 cm^{-1}, i.e. $\nu_{S_1^*-T} = 6700$ cm^{-1}.

The absorption spectrum of 1,2; 7,8-dibenzanthracene (XIV) has a very complex structure, beginning approximately at the same frequency ($\nu_{00} = 25\,309$) as that of 1,2; 5,6-dibenzanthracene. The energy[80] of the $T-S_0$ transition is approximately 17 900 cm^{-1}. The first phosphorescence band[78] is at 18 500 cm^{-1}, i.e. the T level lies 680 cm^{-1} below the S_1^* level (as in the case of 1,2;5,6-dibenzanthracene).

The absorption spectrum of 1,2; 9,10-dibenzonaphthacene (XV) has not been analysed in the literature. It consists of a large number of peaks; the long-wavelength peaks are similar to the absorption band of naphthacene; the first band is at 23 115 cm^{-1}, i.e. approximately at the same frequency as the absorption edge of 1,2;7,8-dibenzanthracene.



Triphenylene (XXXVI). Symmetry D_{3h}. Because of the presence of a third-order symmetry axis the electronic spectra of triphenylene show some specific features. The absorption spectrum has three bands: ^1L_b, ^1L_a, and ^1B_a (the ^1B_a and ^1B_b states are mixtures, as in benzene and coronene[85]). The electronic transitions ^1L_b and ^1L_a are forbidden by symmetry.

Butlar and Grebenshchikov[120] have recently obtained a quasi-linear structure for the $S_1^*-S_0$ and $T-S_0$ spectra in hexane and heptane solutions at 77°K. The 00 transition band at 29 138 cm^{-1}, coinciding in absorption and emission by resonance, was found to be very weak, in accordance with expectations that this band should be forbidden by symmetry. In the long-wavelength absorption spectrum the following vibrational differences were identified: 260, 606, 740, 1026, 1160, 1336, and 1416 cm^{-1}, of which the 1336 frequency is the one most frequently found in combination with other frequencies. The fluorescence spectrum contains more than 50 narrow bands, interpreted in terms of the fundamental frequencies 253, 616, 688, 749, 1048, 1185, 1341, 1430, and 1472 cm^{-1}.

The most characteristic frequency difference is 1341 cm^{-1}. The phosphorescence spectrum begins with a weak band ($\nu_{00} = 23\,587$ cm^{-1}), and has a very complicated structure. Only the differences 735, 1341, and 1430 cm^{-1} can be reliably identified. The polarisation phosphorescence spectrum has a vibrational structure[36].

1,2;3,4-Dibenzanthracene. Symmetry C_{2h}. The absorption spectrum in benzene begins with a weak α band at 3750 Å (26 660 cm^{-1}), which occurs at a shorter

wavelength than in the corresponding 1,2; 7,8- and 1,2; 5,6-isomers. The lower $S_1^*-S_0$ transition is close in energy to that of anthracene but the type of excitation of the electrons may be similar to that in chrysene and 1,2; 5,6- and 1,2; 7,8-dibenzanthracenes. The phosphorescence band has three maxima[78] at 17770, 16330, and 16180 cm^{-1}.

1,2;3,4-Dibenzonapthacene. As the polyacene part of the molecule becomes longer, the electronic bands characteristic of the appropriate polyacene stand out more sharply. The long-wavelength absorption band of 1,2;3,4-dibenzonaphthacene is very similar in structure to the band in naphthacene. The same is true of the spectrum of 1,2;3,4-dibenzopentacene.

The fusion of four benzene nuclei to a polyacene produces a spectrum with a more complicated system of bands.

4. *peri*-FUSED HYDROCARBONS

In some cases it is more reasonable to regard *peri*-fused hydrocarbons as the result of the condensation not of simple benzene rings but of more complicated aromatic nuclei.

Pyrene (XVIII). Symmetry D_{2h}. This hydrocarbon can be regarded as the condensation product of two naphthalene rings. The absorption spectrum has four electronic bands: ^1L_b (ν_{00} = 26900 cm^{-1}), ^1L_a (29500 cm^{-1}), ^1B_b (36400 cm^{-1}), and ^1B_a (41300 cm^{-1}). Theoretical considerations predict polarisation of the ^1L_b and ^1B_b bands along the x axis, and polarisation of the ^1L_a and ^1B_a bands along the y axis. Measurements of polarised fluorescence by Williams[121] revealed that the polarisation is the same for the ^1L_b, ^1L_a, and ^1B_b bands. However, the polarisation spectra obtained by Zimmerman and Yoop[36] confirmed the theoretical predictions. The papers by Shpol'skii and his coworkers[44,45,55,118] describe studies of the structure of the electronic bands. Klimova[55] distinguished three systems of bands in absorption: a system of diffuse bands in the region 2800–2500 Å, a system of second electronic transition bands in the region 3400–3800 Å, and a system of $S_1^*-S_0$ transition bands in the region 3700–3400 Å.

Table 5, compiled from Ref. 55, illustrates the good agreement between the frequencies which are active in vibronic bands and the frequencies obtained from vibrational spectra (infrared and Raman). The possibility of interpreting the vibrational frequencies of the excited states of a molecule is also evident from Table 5.

The activity of vibration frequencies of type b_{1g} has been confirmed experimentally. Zimmerman and Yoop[36] distinguished two series of bands, polarised in mutually perpendicular directions, in the polarisation fluorescence spectrum of an alcoholic solution at -180°C. The main series began with a 00 band at ~26900 cm^{-1}, and the origin of the second series was displaced towards lower frequencies by about 900 cm^{-1}. This difference is close to the frequency of the b_{1g} vibration ($\nu_{b_{1g}} \simeq$ 1106 cm^{-1}); the discrepancy between the observed frequencies arises from the inadequate resolution of the spectral structure in the alcohol solution.

The spectrum of the orange-red phosphorescence of the solutions is found in the region 16900–15250 cm^{-1}. The structure of the phosphorescence spectrum, interpreted using the frequencies 404, 1232, and 1406 cm^{-1}, is most sharply resolved at low temperatures in hexane solution[44,45,55]. The triplet level in the pyrene molecule lies 10000 cm^{-1} below the S_1^* level ($\nu_{S_1^*-S_0} \simeq$ 26837 cm^{-1}), so that the difference in the $\nu_{S_1^*-T}$ frequencies in pyrene is of the same order of magnitude as in the polyacenes. This fact provides evidence in favour of our suggestion regarding the condensation of naphthalene rings. Another surprising fact should be noted: the frequencies of the ^1L_b and ^1L_a 00 bands in the pyrene spectrum are lower than those of the corresponding bands in the naphthalene spectrum by approximately the same amount ($\Delta\nu\,^1L_b$ = 31750 - 26837 = = 4913 cm^{-1} and $\Delta\nu\,^1L_a$ = 34500 - 29500 = 5000 cm^{-1}). A decrease in the frequency of the ν_{00} bands of comparable magnitude is observed when the length of the polyacene chain is increased.

TABLE 5. Fundamental vibrational frequencies (cm^{-1}) of the pyrene molecule[55].

Second excited electronic state		First excited electronic state		Fluorescence spectrum		Raman spectrum		Infrared spectrum		Symmetry type
ν	intensity	ν	intensity	ν	intensity	ν	intensity	ν	intensity	
						349				
392	m.	392	m.	406		406	w.			a_g
454	w.	454	m.	456	m.			456	v.w.	b_{1u}
			s.	498	m.			497	m.	b_{3u}
			m.	559	w.	558	w.			
			m.	590	w.	591	m.	589	w.	a_g
			v.s.	678	w.			675	v.w.	
		722	m.	736	s.			734	m.	
786	w.	782	m.	802	s.					
				945	w.			945	v.w.	
				1028	w.					
				1068	m.	1067	w.			a_g
		1106	v.s.	1107	s.	1108	w.			b_{1g}
				1143	m.	1142	m.			a_g
1162	w.			1183	w.	1184	w.			a_g
1225	w.	1229	v.w.	1232	m.			1283	v.w.	
				1240	w.	1239	v.s.			a_g
						1308				
1327	m.			1325	m.	1327	v.w.			
						1349	w.			a_g
				1366	m.	1369	w.			b_{1g}
				1389	w.					
1393	w.	1394	w.	1405	v.s.	1407	v.s.			a_g
		1468	v.w.	1500	m.	1500	v.w.			
1500	m.	1528	v.w.	1551	m.	1551	v.w.			
				1595	m.	1594	s.			b_{1g}
				1631	m.	1631	v.s.			a_g
						2872	m.			
				3043	w.	3046	m.			b_{1g}

Note. m. = medium; w. = weak; s. = strong; v.s. = very strong; v.w. = very weak.

1,2-Benzopyrene (XIX). Symmetry C_{2v}. The absorption spectrum is fairly similar to that of pyrene in shape and position. Solutions have a violet fluorescence, with a band extending from 3750 to 4500 Å. At 77°K the fluorescence spectrum in alcohol splits into 10 bands, and the spectrum in hexane splits into ~100 bands. The relatively weak, first fluorescence band (ν_{00} = 26570 cm^{-1}) is shifted towards the red by only 300 cm^{-1} as compared with the corresponding band of pyrene. Shpol'skii and coworkers[46] have given a detailed analysis of the fluorescence and phosphorescence spectra in hexane at 77° and 4°K. They identified 32 frequencies in the fluorescence bands, the most active of which are 1254, 1339, 1415, and 1444 cm^{-1}, assigned to fully symmetrical vibrations, and also 772 and 780 cm^{-1}, assigned to not fully symmetrical vibrations. The first four frequencies are intense only in

combination with the last two. The first phosphorescence band ν_{00} = 18 630 cm^{-1} is strong, and is separated from the ν_{00} fluorescence band by 7940 cm^{-1} (on the low-frequency side). Thus, the $\nu_{S_1^*-T}$ difference in 1,2-benzopyrene is lower than in pyrene. In the phosphorescence band, which extends over the region 5330–6700 Å, the following vibrational frequencies have been identified: 343, 383, 456, 649, 1090, 1150, 1255, 1262, 1339, 1415, and 1444 cm^{-1}. The absorption spectra of hydrocarbons consisting of a polyacene group fused to the pyrene nucleus in the 1,2-position can be treated as the sum of the absorption curves of pyrene and the corresponding polyacene. Thus, the long-wavelength absorption band of naphtho(2′, 3′-1,2)--pyrene is very similar in position and vibrational structure to the *P* band of anthracene. A second, very strong band, coincides with the strong β band of pyrene, and the third strong band coincides with the β band of anthracene. In a similar way, the absorption spectrum of 5,6; 15,16--dibenzohexacene can be described by superimposing the bands of naphthacene and pyrene.

3,4-Benzopyrene (XX). Symmetry C_{1h}. The fusion of a benzene ring to pyrene in the 3,4-position produces a more substantial change in the absorption spectrum than with 1,2-benzopyrene. The absorption spectrum begins with a stronger band, at a longer wavelength (4030 Å).

The bright fluorescence spectrum in alcohol and liquid paraffin solutions consists[122] of broad bands, spaced 1390 cm^{-1} apart. In hexane–octane solutions at 77°K these bands split into narrow-band multiplets[44]. Shpol'skii and Klimova[47] made a detailed analysis of the structure of the fluorescence band in heptance and other n-paraffins at 20° and 4°K. The strong component of the purely electronic multiplet is at 4023 Å (24 847 cm^{-1}); the following frequencies are active in the vibrational spectrum: 218, 335, 455, 613, 635, 853, 1111, 1163, 1237, 1345, 1389, 1417, 1586, and 1636 cm^{-1}. Frequency progressions by 1389 cm^{-1} are the most active, and give a characteristic periodicity to the spectrum. This is obviously associated with the same type of skeletal vibration as the 1406 cm^{-1} frequency in pyrene. The phosphorescence spectrum, which begins with a ν_{00} band at 14 670 cm^{-1}, has been described by Muel and Hubert-Habart[119], who report vibrational frequencies of 335 and 1237 cm^{-1}. Addition of a benzene ring to pyrene in the 3,4-position lowers the energies corresponding to $\nu_{S_1^*-S_0}$ and ν_{T-S_0} by the same amount (2000 cm^{-1}). It is surprising that the frequencies of these transitions in 3,4-benzopyrene are the same as in anthracene, despite the fact that the former has two additional benzene rings.

1,2; 4,5- or 3,4; 6,7-Dibenzopyrne (XXI). Symmetry C_{1h}. The absorption spectrum begins with a band at 4280 Å, and is similar to the spectrum of 3,4-benzopyrene, differing from it by a large number of weak, long--wavelength α bands. Although it is generally believed that the absorption spectrum begins at a longer wavelength than that of 3,4-benzopyrene, in fact, the purely electronic fluorescence bands show that the two spectra begin in the same region. A quasi-linear fluorescence spectrum (3900–4300 Å) in n-paraffins at 77°, 20°, and 4°K was obtained and analysed by Shpol'skii and Klimova[49,56]. The strongest component of the purely electronic multiplet in octane is at 25 250 cm^{-1}. 16 frequencies have been identified in the vibrational structure. Most of the fundamental frequencies coincide with those found to be active in the fluorescence spectrum of 3,4-benzopyrene: this follows, in part, from symmetry considerations (the two molecules have the same symmetry type). Fusion of a 6,7-ring to 3,4-benzopyrene produces an increase of ~400 cm^{-1} in the $\nu_{S_1^*-S_0}$ frequency. Unfortunately, there are no data on the position of the triplet level of this molecule. In the writer's opinion, the $\nu_{S_1^*-T}$ difference should decrease in the same way as on going from pyrene to 1,2-benzopyrene; the *T* level can be expected to lie in the region of 17 000 cm^{-1}.

3-Methyl-4,5-ethylene-3,4; 6,7-dibenzopyrene (XXII). The above hypothesis is confirmed by considering the spectra of 3-methyl-4,5-ethylene-3,4;6,7--dibenzopyrene (XXII), an alkyl derivative of the previous hydrocarbon. The structure of the long-wavelength absorption band and of the luminescence bands at 77°K in octane solution has been examined by Khesina[59,60]. Not surprisingly, the saturated five-membered ring and the methyl group produce a small bathochromic shift of the 00 band ($\nu_{S_1^*-S_0}$ 3988 Å, 25 065 cm^{-1}) as compared with 3,4; 6,7-dibenzopyrene. The following vibrational frequencies have been identified in the absorption band: 245, 270, 385, 440, 600, 635, 850, 1236, and 1415 cm^{-1}.

The fluorescence band contains the following frequencies: 251 (s.), 312 (m.), 410 (m.), 445 (s.), **602** (s.), 635 (s.), 854 (s.), 1236 (s.), **1354** (s.), 1415 (s.), and **1633** (s.). (These frequencies have similar values to the strong frequencies of 3,4; 6,7-dibenzopyrene.) The phosphorescence spectrum is shifted by 8600 cm^{-1} towards lower frequencies. It begins with a strong band at 6081 Å (16 450 cm^{-1}), and contains the differences 312 and 602 cm^{-1}, i.e. it occurs in the region which we have suggested for the phosphorescence of 3,4; 6,7-dibenzopyrene. Similar spectroscopic characteristics are to be expected also in another derivative of pyrene 1,2; 3,4-dibenzopyrene (XXIII), a close isomer of 3,4; 6,7-dibenzopyrene.

3,4-Naphtho-6,7-benzopyrene (XXV). Replacement of the benzene ring in the 3,4-position of 3,4; 6,7-dibenzopyrene by a naphthalene ring produces a decrease (to 23 900 cm^{-1}) in the frequency of the lower $S_1^*-S_0$ transition. Khesina[60] described the banded absorption, fluorescence, and phosphorescence spectra of a hexane solution of the compound at 77°K. The absorption spectrum was analysed from the ν_{00} band (23 917 cm^{-1}) in terms of the frequencies 190, 315, 471, 540, 745, 770, 990, 1370, 1430, and 1580 cm^{-1}, and the fluorescence spectrum in terms of the frequencies 205, **280**, **315**, **460**, **635**, 745, 785, 1340, 1440, and 1624 cm^{-1}. (These frequencies are active also in the phosphorescence spectrum.)

3,4,5,6,7-Tribenzopyrene. The frequencies of the $S_1^*-S_0$ and $T-S_0$ transitions in this molecule are not very different from the corresponding frequencies in 3-methyl-4,5-ethylene-3,4; 6,7-dibenzopyrene. The fluorescence band, located in the region 3950–5000 Å, splits (in octane solutions at 77°K) into a large number of narrow bands[60], interpreted in terms of the frequencies **286**, **387**, 415, 500, 690, 1267, 1311, 1410, and 1634 cm^{-1}. (These frequencies are active in the phosphorescence spectrum.) The first phosphorescence band (16 386 cm^{-1}) is separated from the first fluorescence band (25 258 cm^{-1}) by 8872 cm^{-1}. The frequencies 283, 385, 411, 620, and 645 cm^{-1} have been identified[59] in the long-wavelength absorption spectrum.

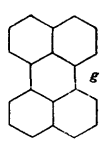
3,4; 8,9-Dibenzopyrne (XXVI). Symmetry C_{2h}. The absorption spectrum of a solution of this compound

begins with a 4510 Å band of medium intensity (a p band according to Clar); the second system extends from 3135 to 2400 Å. Shpol'skii and Klimova[49,56] analysed the structure of these bands in solutions of n-paraffins at 20° and 4°K. Six broad bands (3160–2900 Å) were detected in the region of the second transition. The long-wavelength absorption band with ν_{00} = 22 465 cm^{-1} was interpreted in terms of 17 frequencies, identical in value to frequencies which are active in the fluorescence spectrum. The fluorescence spectrum was interpreted in terms of 19 frequencies: 265 (v.s.), 419 (w.), 508 (w.), 647 (m.), 783 (v.w.), 1096 (w.), 1162 (m.), 1198 (s.), 1241 (v.s.), 1276 (s.), 1332 (w.), 1341 (w.), 1359 (v.w.), 1386 (s.), 1436 (s.), 1567 (m.), and 1632 (w.). The phosphorescence spectrum is shifted 10 425 cm^{-1} towards lower frequencies with respect to the fluorescence spectrum. According to Muel and Hubert-Habart[119] the 00 phosphorescence band is at 12 040 cm^{-1} in toluene, and there are vibrational differences of 280, 1400, and 2610 cm^{-1}. The 3,4; 8,9-dibenzopyrene molecule, like the anthanthrene molecule, can be regarded as the condensation product of two anthracene rings. The large energy difference between the S and T levels is retained, and the frequencies of the S_1^*–S_0 and T–S_0 transitions are close to the corresponding values for anthracene; $\nu_{S_1^*-S_0}$ is lower by about 3800 cm^{-1} than in anthracene and by about 2400 cm^{-1} than in 3,4-benzopyrene.

The absorption spectra of the other pyrene derivatives described in a series of papers by Clar[74–77] vary in a complicated manner with the number and positions of fused benzene rings.

Anthanthrene (XXVII). Symmetry C_{2h}. This molecule can be regarded as the result of the linear cyclisation of naphthalene or anthracene nuclei. The absorption spectrum contains three intense systems of bands: p, β, and β', according to Clar, beginning at 4330 Å (23 100 cm^{-1}). At room temperature[117] the fluorescence band has two maxima: 23 250 and 21 900 cm^{-1} ($\Delta\nu$ = 1350). In the phosphorescence spectrum, 5 bands have been identified. The first is at 11 850 cm^{-1}, the others are separated from it by 360, 740, 1430, and 1650 cm^{-1} respectively[119]. The difference in energies and levels is 11 400 cm^{-1}, i.e. of the same order as in the polyacenes.

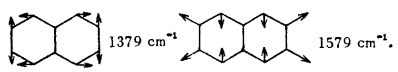
A different mode of condensation of aromatic rings is found in the perylene series.



Perylene. Symmetry D_{2h}. Perylene is readily prepared from naphthalene[73] by *peri*-condensation of naphthalene nuclei. The nuclei retain the π-electron conjugation of naphthalene, because the g bonds are not very different in length from single bonds. However, the absorption properties are vastly different. The frequency of the S_1^*–S_0 transition in perylene is lower than in naphthalene by 9000 cm^{-1}: this shift is greater than for the change from naphthalene to pyrene. The absorption spectrum is characterised by four bands: p, α, α', and β, according to Clar, with 00 transitions at the frequencies 22 700, 29 500, 34 300, and 39 600 cm^{-1} for an alcoholic solution[36] at -180°C (Clar gives[73] 22 800, 29 600, 34 300, and 39 000 cm^{-1}). Platt[84] made a theoretical study of the electronic states of perylene. His calculations gave transition energies different from the experimental values, with identical polarisations for the first three transitions.

The polarisation measurements of Williams[121], and Zimmerman and Yoop[36] showed that the 22 800 and 39 900 cm^{-1} transitions are polarised in mutually perpendicular directions. Hochstrasser[123] concluded that the long-wavelength transition is polarised along the long axis. The quasi-linear structure of the long-wavelength absorption and fluorescence bands (associated with an A_{1g}–B_{2u} transition) in hexane solution at 77°K has been described by Shpol'skii and Personov[48,58]. (The fluorescence spectrum under those same conditions was obtained earlier by Bowen and Brocklehurst[70].)

The strongest component of the multiplet of the purely electronic fluorescence band is at 4454 Å (22 445 cm^{-1}). The absorption bands have been analysed in terms of the frequencies 356, 420, 548, 1290, 1402, and 1604 cm^{-1}, and the fluorescence bands in terms of the frequencies 358, 430, 550, 1298, 1375, and 1578 cm^{-1}. In his analysis of these spectra, Personov[48,57] pointed out the identity of the frequencies of fully symmetrical vibrations which are active in the fluorescence spectra of naphthalene and perylene: 1379 and 1579 cm^{-1}. In the case of naphthalene these frequencies are associated with skeletal vibrations:



According to a calculation[80], the triplet level, or more accurately the frequency of the T–S_0 transition, lies in the region of 12 600 cm^{-1}. The difference between $\nu_{S_1^*-S_0}$ and ν_{T-S_0} amounts to 10 100 cm^{-1}, and is thus comparable in magnitude to the value for linear polyacenes. This is in keeping with the view that perylene is the result of *peri*-fusion of two naphthalene rings.

1,12-Benzoperylene (XXXIV). Symmetry C_{2v}. Since its structure is intermediate between those of perylene and coronene, 1,12-benzoperylene shows significant differences in spectral characteristics from these hydrocarbons. It would seem that addition of a benzene ring to perylene should induce, most probably, a bathochromic shift of the p band. However, although the absorption spectrum begins at λ_{00} = 4065 Å, i.e. at a longer wavelength than in perylene, this absorption is associated[73] with a weak α band ($\log\epsilon$ = 2.7). The stronger p band ($\log\epsilon$ = 4–4.5) lies in the region 3900–3300 Å, and lastly the strongest β band lies in the region of 3000 Å. Ganguly and Mukherjee[124] measured the polarisation of the absorption bands for a single crystal, and showed that the p band is polarised along the long, y axis of the molecule. For the α band, they obtained the ratio I_b/I_a = 1.04, whereas a ratio of 0.015 is expected theoretically for polarisation along the axis. Nevertheless, the electronic transition of the long-wavelength band appears to be polarised along the x axis, and the discrepancy is due to the fact that the band structure is not resolved and contains overlapping vibrational bands polarised at right angles to each other, as in the absorption spectrum of phenanthrene[71] which has the same symmetry as that of 1,12-benzoperylene. Personov[58] was able to resolve and to interpret partly the complex vibrational structure of the long-wavelength absorption, fluorescence, and phosphorescence spectrum in paraffin solutions at 77°K. The 00 fluorescence band in hexane at 4060 Å (24 625 cm^{-1}) is fairly strong. The short-wavelength doublet at 16 258/16 228 cm^{-1} in the phosphorescence

spectrum is separated from the ν_{00} fluorescence band by 8400 cm^{-1}. The decrease in $\nu_{S_1^*-T}$ as compared with perylene and the occurrence of the long-wavelength α band are additional evidence of the similarity of the spectral properties of 1,12-benzoperylene and phenanthrene: 1,12-benzoperylene can be regarded as a dimer of phenanthrene. The dimerisation is accompanied by a decrease in the frequencies of the $S_1^*-S_0$ and $T-S_0$ transitions by 4200 and 5350 cm^{-1} respectively.

Comparison of 1,12-benzoperylene with phenanthrene allows us to understand the difference between its spectra and those of perylene, whose electronic states have peculiarities similar to those of the polyacenes.

Terrylene (XXIX). Symmetry D_{2h}. The *peri*--fusion of three naphthalene nuclei shifts the origin of the absorption spectrum towards longer wavelengths. The first band (5300 Å, 18 860 cm^{-1}) is 4000 cm^{-1} below that of perylene.

1,2-Benzoperylene. The absorption curve is similar to that of perylene, but shifted towards the long--wavelength region (first band at 5140 Å). A similar state of affairs is found with 1,2; 7,8-dibenzoperylene. The origin of the absorption spectrum lies at still longer wavelengths (λ_{00} = 5460 Å). The spectrum of 1,2; 11,12-dibenzoperylene is characterised by an even larger shift. The first absorption band is at 5580 Å (17 920 cm^{-1}).

In *meso*-naphthodianthrene (XXX) two anthracene nuclei are joined by three bonds in the *peri*-position. The long-wavelength absorption band is at 6625 Å (15 090 cm^{-1}). The frequency of the $S_1^*-S_0$ transition is 10 000 cm^{-1} lower than in anthracene, i.e. of the same order as on going from naphthalene to perylene.

1,14-bisanthene (XXXV). In this compound the initial λ_{00} band is at 6350 Å (15 740 cm^{-1}), 700 cm^{-1} higher than in *meso*-naphthodianthrene. The increase in the $\nu_{S_1^*-S_0}$ frequency is similar to that found in the spectra of the perylene–1,12-benzopyrene pair.

Coronene (XXXVII). This molecule has the same D_{6h} symmetry as the benzene molecule. This predetermines many of its general spectral properties. Three bands are distinguished in the absorption spectrum: ^1L_b, ^1L_a, and $^1B_{ab}$. Calculation showed that the $^1A-^1L_b$ and $^1A-^1L_a$ transitions are forbidden by symmetry, whereas the $^1A-^1B_{ab}$ transition is allowed. Mentzel and Zimmerman[38] gave a vibrational analysis of the absorption and luminescence bands of a solution of coronene in a mixture of tetrahydrofuran, alcohol, and ether (11 : 14 : 1) at 90°K. The structure of the $^1B_{ab}$ band (λ_{00} = 32 900 cm^{-1}) was analysed in terms of the differences 500, 1400, and 1700 cm^{-1}, the second frequency giving rise to the main series. The differences 500, 1000, 1200, 1350, and 1500 cm^{-1} were identified in the ^1L_a band, which extends from 28 850 to 32 400 cm^{-1}. The last two give rise to series. The ^1L_b band (ν_{00} = 23 500 cm^{-1}) was interpreted in terms of the frequencies 350, 650, 1250, 1350, 1450, and 1600 cm^{-1}. The series are determined by the frequencies 1350 and 1600 cm^{-1}. It has also been shown that the absorption bands of 1,12-benzoperylene, which is usually present as an impurity in coronene, appear in the spectrum. Bowen and Brocklehurst obtained a quasi--linear structure from the luminescence spectra of coronene in hexane at 77°K, and also noted the presence of the fluorescence bands of 1,12-benzoperylene, present as an impurity[70]. Shpol'skii and coworkers[44] published a detailed vibrational analysis of the fluorescence spectrum of coronene, which consists, in hexane at 77°K, of sharp doublets beginning at 23 543/23 456 cm^{-1}. These workers pointed out the active status of the "breathing" frequency of the benzene ring (992 cm^{-1}) and of the symmetrical stretching vibration of the C–H bonds (3070 cm^{-1}). Sidman[125] analysed the fluorescence spectrum in hexane at -180°C and assigned the 320 and 1400 cm^{-1} frequencies to vibrations of e_g^+ symmetry. Mentzel and Zimmerman[38] interpreted the fluorescence spectrum, consisting of 24 bands with an initial band at 23 500 cm^{-1}, in terms of the frequencies 350, 650, 1000, 1250, 1450, and 1600 cm^{-1}. They observed a constant polarisation along the entire fluorescence spectrum.

The phosphorescence spectrum of the compound in the crystalline state was studied at 77°K by Clar and Zander[78], in a mixture of propyl ether and isopentane at 90°K (ν_{00} = = 19 410 cm^{-1}) by Czekalla and Mager[103], in hexane and heptane at 77°K (ν_{00} = 19 375) by Shpol'skii and Klimova[50], and in alcohol at 90°K (ν_{00} = 19 400) by Dörr and Cropper[40]. A detailed analysis of the structure, using the best spectral resolution[50], led to the identification of the fundamental frequencies 120, 365, 850, 1157, 1226, 1350, 1405, 1435, 1618, and 1630 cm^{-1}. The polarisation phosphorescence spectrum shows a large change of polarisation along the spectrum[40]; this indicates the occurrence of not fully symmetrical vibrations whose frequencies, however, were not identified. It should be noted that in a mixed crystal with perhydrocoronene, delayed fluorescence (due to the return of the molecule from the T to the S_1^* state followed by $S_1^*-S_0$ radiation) is observed for coronene in addition to phosphorescence[23,126]. Zander[127] found that, on increasing the temperature, the relative intensity of the $T-S_0$ emission decreases, whilst the delayed fluorescence increases. So far coronene is the only hydrocarbon for which this type of delayed fluorescence has been observed. This is because the energy difference between the S_1^* and the T states is least in coronene: $\nu_{S_1^*-T}$ = 4100 cm^{-1}. Such a large drop in $\nu_{S_1^*-T}$ arises because in this molecule the angular cyclisation of benzene rings proceeds to a complete cycle.

The spectral features of fused polycyclic hydrocarbons containing a five-membered ring are discussed below using fluorene and fluoranthene as examples

Fluorene (XXXIX). Symmetry C_{2v}. The molecule has the π-electron system of the biphenyl nucleus, the $-CH_2-$ bridge affecting the energy of electronic transitions like an alkyl substituent. The long-wavelength $S_1^*-S_0$ transition is polarised, as in the biphenyl molecule, along the C–C bond linking the benzene rings[128]. There are papers giving an analysis of the vibrational structure of the long-wavelength absorption band of fluorene in the crystalline state[61,128] and in frozen solutions[61]. The resonance band in absorption and fluorescence is at 33 160 cm^{-1} (in heptane). The fluorescence band spectrum of the crystals has also been described; it has been shown[128] that the frequencies 404 and 564 cm^{-1} give rise to strong series of bands for fully symmetrical vibrations, polarised along the short axis of the molecule. Nurmukhametov and Gobov[61] described also the fluorescence and phosphorescence band spectrum of a heptane solution at 77°K. The structure of the phosphorescence band of a cyclohexane solution of this compound has been described[69]. The purely electronic

phosphorescence band (23 786 cm^{-1}) lies 9374 cm^{-1} below the first fluorescence band.

Fluoranthene (XXXVIII). Quasi-linear luminescence spectra have been obtained by Val'dman and Sheremet'ev[129] at 77°K in heptane. The vibrational frequencies 226, 343, 556, 792, 908, and 1614 cm^{-1} in the blue fluorescence band were identified with ν_{00} = 24 521 cm^{-1}. The orange-red phosphorescence spectrum begins with a band at 18 416 cm^{-1} and contains the frequencies 343, 556, 792, 1175, 1310, 1420, and 1614 cm^{-1}. The difference between the S_1^* and the T levels is 6105 cm^{-1}; cyclisation of benzene rings around a five-membered ring lowers this difference, just as it does in the case of cyclisation around a benzene ring (triphenylene, coronene). Lastly, we shall consider the work on the structure of the spectrum of azulene, which consists of two condensed rings (one five- -membered and one seven-membered).

The hydrocarbon azulene has unusual properties: being coloured, it shows ultraviolet fluorescence[130-133]. It has been shown that the fluorescence is due to emission from the second excited singlet level, whereas excitation in the first absorption band does not cause luminescence[130]. Ruzevich[133] obtained a well resolved vibrational structure of the fluorescence band in hexane solution at 77°K.

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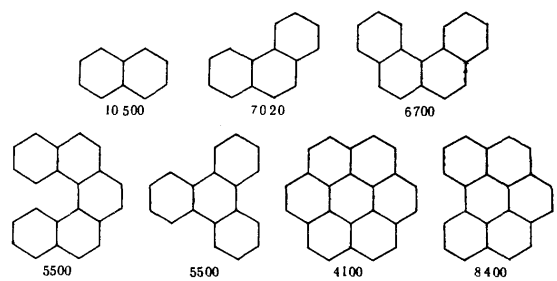
We shall now consider the correlations which have been established empirically between the position and the structure of the electronic bands. An increase in the length of the π-electron system in the polyacene series (naphthalene, anthracene, naphthacene, pentacene, hexacene) causes a monotonic decrease in the energy of the long-wavelength $S_1^*-S_0$ and $T-S_0$ transitions by the following amounts: 5500 (6370 for ν_{T-S_0}), 5080 (4430), 4000 (2500), and 3000 cm^{-1}. As will be clear from the subsequent discussion, the decrement in $\nu_{S_1^*-S_0}$ and ν_{T-S_0} frequencies per benzene ring is largest in the polyacenes, with an average value of 5000 cm^{-1} for the first few members. All the polyacenes, beginning with anthracene, have a "*p* band", with a very similar coarse vibrational structure. This similarity arises because one of the frequencies in the region 1400 cm^{-1} is predominant. The difference in position between the S_1^* and T levels, amounting to some 10 000 cm^{-1}, is hardly affected by an increase in the number of condensed rings in the polyacene series (see Table 3). Molecules which can be regarded as formed by the condensation of more complicated aromatic nuclei also show this type of spectral peculiarity. Thus, the pyrene molecule is obtained by the linear condensation of two naphthalene nuclei, the molecule of anthanthrene can be derived from two anthracene or three naphthalene nuclei, and the molecule of 1,12-benzoperylene from two phenanthrene molecules. The energies of the $S_1^*-S_0$ and $T-S_0$ transitions in the spectra of the pairs of compounds naphthalene–pyrene, anthanthrene–anthracene, and 1,12-benzopyrene–phenanthrene differ by the following amounts respectively: 4900 (4400 for $T-S_0$), 3000 (3000), and 4200 (5550) cm^{-1}. Thus, fusion of the more complicated aromatic nuclei lowers the frequency of the electronic bands by about the same amount as in the polyacenes, despite the fact that the number of benzene rings in the molecule is increased by more than unity. The difference between the frequencies $\nu_{S_1^*-S_0}$ and ν_{T-S_0} also stays practically constant in condensation of this type: in pyrene and anthanthrene $\nu_{S_1^*-T}$ equals 9900 and 11 400 cm^{-1} respectively. *Peri*-condensation of naphthalene and anthracene nuclei (as in perylene) lowers the frequencies of the long-wavelength bands more significantly than in the pyrenes. However, this decrease is less than in the polyacenes when calculated for a single ring. Again, the frequency difference between $\nu_{S_1^*-S_0}$ and ν_{T-S_0} is found to be constant (in perylene $\nu_{S_1^*-T}$ = 10 000 cm^{-1}). When π-electron groups are conjugated in an open chain, as in the polyphenyls and diphenylpolyenes, the decrease in $\nu_{S_1^*-S_0}$ frequency per unit of the conjugated system is smaller than in the polyacenes by about a factor of two. In these classes of compounds, phosphorescence has been observed only for biphenyl, in the spectrum of which the $\nu_{S_1^*-T}$ difference amounts to 10 000 cm^{-1}.

A different type of spectral changes is observed for angularly condensed hydrocarbons. Fusion of a benzene ring to a polyacene molecule in the 1,2-position causes a much smaller shift of the long-wavelength origin of the absorption spectrum. The α bands are more affected than the p bands, which keep their position unchanged in the benzopolyacene series. As a result, the α band becomes the long-wavelength band in some benzopolyacenes instead of the p band (the long-wavelength band in the corresponding polyacenes). In benzopolyacenes with a long polyacene chain the shift is insufficient, and the p band retains the long-wavelength position and is very similar to the p band of the polyacene. Also, angular condensation decreases the difference between the S_1^* and T levels: in phenanthrene this difference drops to 7080 cm^{-1}, in benzanthracene to 9500 cm^{-1}. Angular fusion of two or more benzene rings to the end rings of polyacenes increases the tendencies noted for the monobenzopolyacenes. In 3,4-benzophenanthrene the difference drops to 6700 cm^{-1}, in triphenylene to 5500 cm^{-1}. The maximum degree of angular cyclisation occurs in coronene, and this coincides, characteristically, with a minimum value of the difference $\nu_{S_1^*-T}$ (4100 cm^{-1}). The decrease in the difference $\nu_{S_1^*-T}$ is clearly illustrated by the series



It must be emphasised that 1,12-benzoperylene is not included in this series because it is regarded as the result of the linear condensation of two phenanthrene molecules.

Essentially, this series spans the whole range of $\nu_{S_1^*-T}$ values met in aromatic hydrocarbons (from 12 000 to 4000 cm^{-1}). The rule relating the relative positions of the S_1^* and T levels to the structure of the π-electron system of the molecule enables us to predict the region in which the phosphorescence spectrum of aromatic hydrocarbon molecules can be expected to occur from a knowledge of the absorption or fluorescence spectrum. A knowledge of the position of the S and T levels and of the

absorption and luminescence spectra of aromatic hydrocarbons as a function of molecular structure is valuable from many points of view. Several of these compounds show photochemical activity, being particularly susceptible to photo-oxidation. The majority of the reactions proceed through a metastable triplet state. Zander[134] pointed out that a hydrocarbon becomes more and more unstable as the energy of the triplet level drops. Pentacene and hexacene react almost like free radicals. Hexacene is readily oxidised, and reacts instantaneously with maleic anhydride, which decolourises it. Octacene and nonacene appear to be true biradicals. The higher relative position of the T level in angularly condensed hydrocarbons accounts for their high stability as compared with the acenes containing the same number of benzene rings. Many hydrocarbons form photo-oxides under illumination in the presence of oxygen. Using the well-known photo-oxidation of anthracene solutions as an example, it was shown[135] that formation of the photo-oxide involves the participation of a T state. In view of published statements that the T states of organic molecules are promising routes to the realisation of efficient lasers[136,137], it may be useful to assess the possibilities offered by aromatic hydrocarbons. On the whole, these compounds are not very promising. The phosphorescence of all the hydrocarbons examined is characterised by glow-decay times between 0.1 and a few seconds. Most of them have triplet–triplet absorption bands overlapping the absorption spectrum of the S_1^*–S_0 transitions. The phosphorescence yield is no more than one-half of the luminescence yield. Lastly, the Stokes losses during excitation are large.

Many aromatic hydrocarbons show carcinogenic properties, which were originally ascribed to the luminescence of these materials but are now regarded as being associated with the position of the levels. Muel and Hubert-Habart[119] found no unique correlation between the position of the T level and the carcinogenic activity of aromatic hydrocarbons. Attempts have also been made to correlate carcinogenic action with the electron donor or acceptor properties of the molecules[138], again without real success. This property of the molecules does not appear to be determined by a single molecular parameter, but rather by a combination of parameters.

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IONIC AND ELECTRONIC PROCESSES OCCURRING IN CONDENSED HYDROCARBONS UNDER THE INFLUENCE OF IRRADIATION

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I. INTRODUCTION

In the present review we shall discuss the "ionic aspects" of radiolysis, that is, we shall attempt to follow the fate of the charged particles which are formed by the action of radiation and to clarify their chemical role in radiolysis. Particular attention will be paid to the condensed phase, because ionic processes in the gas phase have already been widely investigated and their role in chemical reactions induced by radiation is fully recognised. Studies of the ion–molecule reactions, discovered in 1952 by Tal'roze and coworkers, have made an important contribution to the solution of this problem: they deal with the fundamental chemical process following the formation of the ions. Several review articles[1-4] have appeared on this topic, and we shall not discuss it here in detail. Ionic processes in a condensed phase cannot, as a rule, be investigated under model conditions, as for example in the ionisation chamber of a mass spectrometer, commonly used to study ion–molecule processes in the gas phase. We shall often be compelled, therefore, when discussing various processes involving ions, to use analogies with the gas phase and to carry over to the condensed phase the relationships obtained for gaseous systems. This approach is justified when dealing with the radiolysis of organic compounds, whose molecules experience only weak mutual interactions in a condensed phase and behave in a number of respects as if they were in a rigid gas.

The action of penetrating radiation (gamma quanta, X-rays, or electrons) on matter is mainly the result of interactions between the fast primary quanta or electrons and the electrons located in the electronic shells of atoms or molecules. Interactions between primary particles and atomic nuclei can be ignored in radiation-chemical investigations.

With gamma energies of the order of 1 MeV, the fundamental primary process is Compton scattering, which gives rise to fast electrons in the irradiated material. In contrast to external irradiation with electrons, the Compton effect leads to a uniform irradiation of the material, since

it is equivalent to a number of electron sources distributed throughout the bulk.

Irrespective of the nature of the primary radiation, the active particles are essentially fast electrons. At the very beginning of their residence time in the material these electrons have an energy distribution not very different from the initial energy of the penetrating radiation. However, the number of electrons in the material quickly rises as a result of ionisation, and a wider distribution is rapidly set up. At equilibrium, the energy distribution of the electrons covers a spectrum from well below the ionisation energy of the molecules to a value equal to the original energy of the electrons [5].

The cross-sections for the ionisation and excitation processes occurring under the influence of electron impact are a function of the energy of the electrons. A common feature of all these processes in the high-energy region is a decrease in cross-section with increase of energy. However, the radiation yield of ions, or the ratio of the energies expended in ionisation and in excitation, which determines the yield, remains constant [6]. The ratio depends mainly on the distribution of excited states and on the position of the ionisation level in relation to this distribution. Some typical values of mean energies needed to generate electron–ion pairs in gases [7] are listed in Table 1.

Since the lowest electron energies I which will cause ionisation lie in the range 12–15 eV, we conclude from Table 1 that approximately 40–50% of the total irradiation energies listed goes into ionisation processes†. There is no reason to believe that this proportion decreases in a condensed phase. Indeed, electrons in molecules have practically identical energy spectra in the gas phase and in a condensed phase, and the ionisation energy is actually lowered in a condensed phase by the polarisation of the medium caused by the distributed charges [8]. The subsequent fate of the electrons and ions which are formed is the main problem. If they mutually recombine in a time so short that alternative processes involving the ion and the electron cannot compete, there will be no chemical manifestation of the ionisation process. The excited molecule formed by the recombination can be treated as the true forbear of all chemical transformations in the material. This suggestion was first put forward by Samuel and Magee [9], and has since caused the role of ions and their reactions in a condensed phase to be occasionally underrated. If the recombination of the ion and the electron is slower than some other reaction between these charged particles and a third body, ionic reactions can be expected to play an important part in the radiation-chemical processes in condensed media.

TABLE 1.

Molecule	H_2	N_2	O_2	Air	CO_2	CH_4	C_2H_6	C_2H_4	C_3H_8
Mean energy per ion pair, W, eV	36.3	34.9	30.8	33.9	32.8	27.3	24.5	26.1	25.7
Ratio W/I	2.35	2.24	2.55	—	2.38	2.10	2.10	2.48	2.25

† We should note also that the ions can be formed in an excited state, and that this will increase still further the percentage of the energy used by ionisation processes in the primary act.

The generation, motion, and recombination of ions and electrons in a condensed phase is revealed most directly by studies of the electrical conductivity induced in solids or liquids by irradiation. However, conductivity studies alone are insufficient to characterise the chemical role of the ions.

A number of recent papers have dealt with the direct observation of the ionic processes leading to chemical changes in the material, and have stressed the importance of ionic reactions during radiolysis. The most fundamental among these will be discussed below.

We shall deal first of all with studies of the physical properties of the ions formed during radiolysis. The chemical transformations of the ions will be considered next.

II. ELECTRICAL CONDUCTIVITY UNDER THE INFLUENCE OF IONISING RADIATION

1. Free and Bound Charges

The appearance of electrical conductance in a condensed phase under the influence of ionising radiation is evidence that ions and electrons are formed. The pair of charges produced by the ionisation of a molecule can contribute to the current flowing through a specimen in an electric field only if the positive ion and the electron of which it is composed do not recombine with one another. We shall refer to such electrons and ions as "free". The electron ejected by ionisation suffers collisions as it moves away from the ion, and loses its energy. If the kinetic energy of the electron is converted into thermal energy before the electron has moved to such a distance from the ion as to make the coulombic interaction energy between their charges small, the cold electron can turn back and neutralise "its own" ion. There will then be no contribution to the electrical conductivity. Some of the electrons, having a high initial energy, will be able to move to greater distances from their parent ion, and become free. For free electrons the recombination can involve any positive ion with equal probability. Obviously, the yield of "free" electrons will depend on the rate at which energy is lost by the slow electrons in the medium. An approximate calculation of the maximal energy losses consistent with the escape of an electron of initial energy E from the sphere of coulomb attraction can be made as follows.

Let δ be the fraction of its energy which an electron loses at each collision. The number of collisions needed to cool an electron from energy E to kT is then given by

$$j = \frac{1}{\delta} \ln \frac{E}{kT}$$

and the corresponding time is

$$\tau = \frac{j}{N\sigma v} = \frac{1}{\delta N \sigma v} \ln \frac{E}{kT},$$

where N is the concentration of scattering centres, σ the scattering cross-section, and v the mean velocity of the electron. "Freeing" of the electron requires that the diffusion length after time τ should be greater than or equal to the radius of the sphere of action of the coulombic field $r_c = e^2/\epsilon kT$, that is:

$$\frac{\sqrt{j}}{N\sigma} \geqslant r_c \quad \text{or} \quad \delta \leqslant \frac{(\epsilon kT)^2 \ln \frac{E}{kT}}{e^4 (N\sigma)^2}.$$

Taking the mean free path of the electron to be $\lambda = 1/N\sigma = 5$ Å, with $\epsilon = 2$ and $E = 10$ eV, we find $\delta \leq 1.8 \times 10^{-3}$.

Although this estimate takes no account of the drift of the electron in the coulombic field and is therefore only a rough approximation, it does nevertheless show that the δ values required to free the electrons lie very close to the relative energy losses occurring in the elastic scattering of electrons. We can therefore expect a strong correlation between the yield of free electrons and such parameters of the material as the dielectric constant, crystallinity, and vibrational spectrum.

When solids are irradiated at low temperatures the yield of free electrons should increase with dose of radiation, because stabilised charges accumulate in the material as the dose is increased and the spheres of action of their coulombic fields begin to overlap [10]: under these conditions the electrons need only travel a smaller distance from "their own" ion in order to "free themselves".

Studies of electrical conductance are concerned only with "free" electrons and ions, but they reflect also the behaviour of other charges produced during ionisation.

2. Liquids

Measurements of the yield of charges under the influence of ionising radiation have been made mostly in the liquid phase. The currents in liquid ionisation chambers, and their variation with applied electric field, have been measured. It was expected that at high applied fields all the free carriers would reach the electrodes, and the saturation current under these conditions would be a measure of the rate of formation of charges. It was found, however, that although the current through a liquid ionisation chamber increases more and more slowly as the potential is increased, it never reaches saturation. This happens when the current through the chamber varies linearly with the intensity of irradiation, showing that the charges are destroyed only at the electrodes [11]. Hence, one method of determining the yield was to extrapolate this current to an infinitely large field, because the absence of saturation suggested that some other mechanism was operative and competed with the separation of the ions. This method was used to estimate the ion yield of CS_2, [12,13] and also in some liquid saturated hydrocarbons [14] between C_6 and C_{10}. Yields equal to those in the gas phase [13], or close to them [14] (~ 1), were obtained. Obviously, a method involving such a long extrapolation cannot give precise values for the yield, but estimates by this method are capable in principle of giving the total yield of charges formed during irradiation. It is suggested in these papers that the lack of saturation is due to fast recombination of the charges in the tracks, where the ion density is high. An alternative mechanism, which would have a similar effect, is the recombination of the electrons with "their own" ions.

A second group of papers deals with conductance studies at low field intensities [11,15,16]. Under these conditions only a small fraction of the current carriers reach the electrodes, and the free ions and electrons are lost in the bulk. To calculate the radiation yield $G(e)$ one measures the electrical conductivity $\sigma = n\mu e$, where n is the steady-state concentration of current carriers and μ is a mobility defined as the sum of the mobilities of ions and electrons. The steady-state concentration of current carriers n is determined by the rates of recombination and of generation of free charges:

$$n = \left(\frac{GI}{100} \cdot \frac{1}{k}\right)^{1/2}.$$

Here I is the energy of the radiation in eV absorbed by 1 cm³ of the liquid per second and k the recombination coefficient. The latter can be calculated either from the mobility, $k = (4\pi e/\epsilon)\mu$, or determined experimentally from the kinetics of the decay of σ following removal of the irradiation. The mobility of the ions in the liquid under study must be known in order to calculate G. The most direct method of determining the mobility is to measure the time T required for the ions or electrons to travel the known distance l between the points of generation and of detection. The relationship is $\mu = l/TE$, where E is the strength of the field causing the motion of the current carriers. This method has been used to measure the mobility of ions in n-hexane [15,17]. Some values of μ are set out in Table 2.

The temperature variation of the mobility of electrons, measured [17] by emission from a photocathode into n-hexane under the influence of light, has been found to be exponential with an activation energy of 0.14 ± 0.02 eV. This result suggests that an electron in a liquid may spend part of its time in states which are similar to shallow traps in crystals.

The radiation yields of "free" current carriers measured at low field intensities are smaller than in gases; the following values have been reported: 0.2, [11] 0.09, [15] 0.07. [16] These low values are evidence that only a small fraction of the electrons produced manage to escape from "their own" ions. A recent calculation [21] has shown that the low yield can be satisfactorily explained by assuming that ionisation is brought about only by δ-electrons with an energy of 100–200 eV.

TABLE 2.

Current carriers	μ, cm² V⁻¹ s⁻¹ at 300°C				
Positive	—	$5.8 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$	—	$3.8 \cdot 10^{-4}$
Negative	10^{-3}	$9.2 \cdot 10^{-4}$	$13 \cdot 10^{-4}$	$12.5 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$
Reference	18	19	20	17	15

3. Solids

The appearance of free charges in a solid organic material under the influence of irradiation is accompanied by an increase in electrical conductivity. Since the majority of radiation-chemical investigations have been carried out on amorphous or microcrystalline organic materials, a rigid application of the band theory is not possible. However, as a matter of convenience in the present discussion, the band diagram can be replaced by an energy diagram showing the distribution of levels corresponding to the ionised states. The minimal energy needed to produce a free electron in an organic material is sometimes called the ionisation potential in the condensed phase. This quantity [8] is lower than the ionisation potential in the gas phase by the polarisation energy $2P$ gained

by bringing the two charges from a vacuum into the condensed phase‡. If the molecules of the material have a positive electron affinity Q, the lowest energy consistent with the formation of a pair of charges not interacting with each other is given by

$$E = I_{gas} - 2P - Q = I_{solid} - Q.$$

The energy diagram of the ionised states in the gas phase and in a condensed phase is shown in Fig. 1. In the "forbidden gap", that is, in the band of levels located between the level of the positive ion of the parent substance and that of the negative ion, we can find ionised states whenever impurity molecules with a lower ionisation potential or a higher electron affinity than the molecules of the major constituent are present in the system. Such levels can be produced also by structural defects. Levels in the "forbidden gap", by which electrons or positive charges can be captured, are usually called traps. In principle, the following can take part in electrical conduction: (1) electrons which are not localised on any molecule, (2) electrons captured by the molecules of the material and undergoing resonance charge transfer of negative ions (for molecules with a positive electron affinity), and (3) positive charges in the molecules of the material undergoing resonance charge transfer of ions. In addition, electrical conduction can, on occasions, result from the transport of

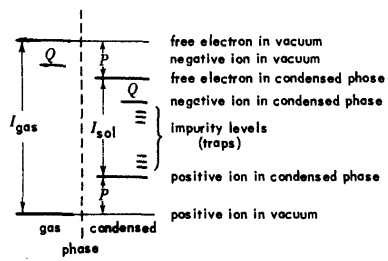


Fig. 1. Energy diagram for ionised states in the gas phase and in a condensed phase.

the ions themselves (either traps which have captured an electron or a hole or charged molecules of the major constituent).

The study of the electrical conductivity of organic substances under the influence of ionising radiation bears some similarity to the study of the photoconductivity of semiconductors and dielectrics. However, in contrast to the effect of light, radiation produces not only current carriers but also new molecules in the host material which can act as traps for the current carriers.

Studies of the electrical conductivity of solid organic materials, and particularly of polymers, have been described in numerous publications [25-33]. The main characteristic of the electrical conductivity observed under irradiation is a dependence of σ upon the dose rate (or intensity) I. In general, it is found that

$$\sigma = n\mu e = \alpha I^{\Delta} \S \qquad (1)$$

where Δ can have any value from 0.5 to 1. The value of Δ is determined by the mechanism of recombination of current carriers. Many solid organic substances give $\Delta \simeq 1$ on irradiation, and $\sigma = 10^{-18} I$ to within two orders of magnitude [34], where σ is expressed in Ω^{-1} cm^{-1} and I (the dose rate) in rad min^{-1}. Ionic conductivity does not appear to play a major role when solid organic substances are irradiated, as evidenced by measurements of the electrical conductivity induced by irradiation in solid heptane [10,35] and polyethylene [33] at liquid nitrogen temperature, when ionic motion is excluded. The electronic conduction processes described by Eqn. (1) are in satisfactory agreement with the theory of photoconduction in the presence of traps [36]. Fowler [37] was the first to apply this theory (to irradiated polyethylene): his scheme describing the participation of traps in the recombination process (scheme *I*) is reproduced in Fig. 2. The figure also shows alternative schemes by which traps can be involved in electrical conduction processes (*II* and *III*). In the first scheme we can assume, to simplify matters, that only the electrons are mobile. In all schemes the electrons, which take part in electrical conduction as long as they remain in the free (non-localised) state, are removed from the sphere of action for appreciable periods when they fall into traps. The time during which they remain untrapped, in the free state, determines their mean effective mobility μ_{eff}, which characterises the electron throughout its lifetime from generation to recombination with a positive ion¶. The extent of filling of the traps is determined by the probability of electrons falling into the traps and by the time of residence of an electron in the trap. As the traps are gradually filled, the electron mobility μ_{eff} increases. If the electron traps are distributed in depth, it is evident that at equilibrium under irradiation the deeper traps will be filled to a greater extent than the shallower traps. The total number of filled traps will depend on the intensity of irradiation, and increase with

‡ In a condensed phase, as in the case of gases, we must distinguish between the "vertical" and the "adiabatic" ionisation potential. The former is determined by an electronic transition in the molecule, and by the electronic polarisation in the medium, without any change in the position of the nuclei of the ionised molecule or of the molecules of the surrounding medium. The adiabatic ionisation potential in a condensed phase is lower than the vertical potential not only because of the different internuclear distance in the resulting ion, but also because of low-frequency polarisation of the medium when polar groups are present. A vertical transition occupies a time of the order of 10^{-15}–10^{-16} s, and is produced by electron impact ionisation or ionisation by light quanta. The low-frequency polarisation is set up, according to the properties of the medium and the temperature, in a time of 10^{-11}–10^{-13} s after the appearance of charges in the medium, and has the effect of placing the electrons and the positive charges in polarisation wells of a peculiar kind. The term polarons has been proposed in the theory of dielectrics for electrons of this type [22]. In polar media such as water and alcohols, polarons (solvated electrons) have been detected experimentally [23,24].

§ In general, electrical conduction involves both electrons and "holes". The latter term refers to positive charges which are mobile by virtue of resonance charge transfer processes. Hence, $\sigma = \mu_h n_h e + \mu_e n_e e$. In order to simplify the problem, it is often assumed that the contribution of carriers of one type can be ignored in comparison to that of carriers of the opposite sign, so that $\sigma = \mu n e$, where n is the concentration of carriers whose contribution to electrical conduction is the more significant and μ their mobility.

¶ When using the mobility μ_{eff}, the expression for the electrical conductivity becomes $\sigma = \mu_{eff} n_n e$, where n_n is the concentration of all negative charges in the material.

increasing intensity. This, in turn, will raise the electron mobility μ_{eff}. Thus, an increase in radiation intensity will, on the one hand, decrease the lifetime of the current carriers by increasing the probability of electron–ion recombination, and on the other hand it will increase the effective mobility of the current carriers. These factors are very sensitive to the distribution of the traps in depth. Thus, in scheme *I* of Fig. 2 we can assume an exponential distribution in depth[37]: this gives the number of traps lying in the range from E to $E + \Delta E$ below the free-electron level as

$$M_E dE \sim e^{-E/kT_i}\ dE,$$

where T_i is a constant characteristic of a particular substance. It turns out that $\Delta = T_i/(T + T_i)$. By suitable choice of T_i we can have any value of Δ from 0.5 to 1, but this value remains constant over a wide range of radiation intensities. The lack of dependence of Δ upon I is the strongest argument in favour of the choice of an exponential energy distribution for the traps.

A relation of the type $\sigma = \alpha I^{\Delta}$ can be obtained if all the traps in the system lie at the same depth. However, the value of Δ will then vary with intensity of irradiation. Thus, at very low intensities, when the lifetime of a current carrier is much greater than its trapped time, $\Delta = \frac{1}{2}$. At high intensities Δ tends towards unity, but it drops back to $\frac{1}{2}$ when most of the traps are filled. The large range of intensity values which has to be covered in order to observe the slow variation of Δ with I does not allow us to identify the type of distribution of the traps with confidence from the measured values of Δ alone: experimental measurements of this quantity usually fall somewhere between 0.5 and 1 and appear to be constant at this intermediate level[38]. For polyethylene it is reported[37] that $\Delta = 0.7$.

If the positive charges formed by irradiation are mobile, electrons captured in traps can recombine with the positive charges directly, without being emitted into the conduction band. This scheme is shown in Fig. 2, *II*. Lastly, we can have a third type of electrical conduction process, shown in Fig. 2, *III*, in which a current carrier is emitted from a deep trap to the conduction band as a result of energy transfer from the radiation field.

We cannot make an unambiguous choice between the various schemes of carrier recombination and trap filling on the basis of measurements of the quantity Δ. Measurements of the kinetics of the growth or decay of electrical conductivity following exposure to or removal from irradiation are also of little help, because any of the models can be made to agree with experiment by suitable choice of distribution of the traps.

The most important conclusion to be drawn from studies of electrical conductivity is that the role of traps in the recombination of free electrons is established. By assuming an exponential energy distribution of traps it has been possible to estimate the concentration of traps present in polyethylene[37] and in octacosane[39] before irradiation. Since this concentration was found to be independent of the degree of purification of the material, it was concluded that traps in saturated hydrocarbons are not impurities but structural defects (possibly perturbations in the short-range order in the molecular distribution[39,40]). The concentrations of traps were found to be very large ($\sim 10^{20}$ cm^{-3}).

4. Accumulation of Stabilised Charges Under Low-Temperature Radiolysis

The discovery of thermally stimulated currents in saturated hydrocarbons irradiated at low temperatures[41–43] is a direct proof of the accumulation of current carriers in traps. The thermally stimulated current peak shown in Fig. 3 appears when irradiated specimens are allowed to warm up and is associated with the emission of current carriers from the traps and their recombination. The appearance of conductance on heating irradiated specimens suggests that both negative and positive charges are stabilised at low temperatures.

The role of traps in recombination processes has been investigated by attempting to introduce new traps into the specimen and monitoring changes in electrical conductivity under irradiation. Thus, Wintle[44] examined the changes in the nature of the σ–I relationship for polyethylene brought about by previous exposure of the specimen to a large dose of radiation. The relationship was found to become linear, with $\Delta = 1$, in keeping with the formation of deep traps as a result of irradiation. The nature of these traps was not characterised. Yakovlev and Frankevich[10] studied the electrical conductivity of n-heptane at liquid nitrogen temperature as a function of irradiation with a constant flux of fast electrons, and found that σ under irradiation falls as the total dose of radiation is increased. They were able to relate this drop in σ to the known concentration of free radicals which had accumulated in the specimen under the

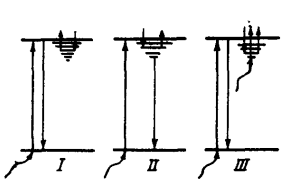


Fig. 2. Distribution of trapping levels and recombination mechanism:
I) recombination of a free electron with an ion; thermal emission of electrons from the traps; II) recombination of an electron captured in a trap with a mobile positive charge; III) recombination of free electrons with ions; excitation of trapped electrons by the transfer of radiation energy.

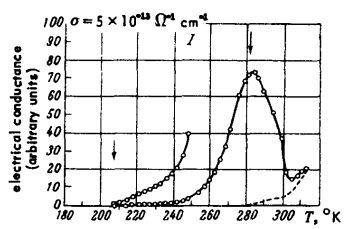


Fig. 3. Thermally stimulated conductance curve in an irradiated paraffin[41,42], dose 50 Mrad. The broken line shows the electrical conductance of the paraffin in the absence of irradiation. The initial section of the curve is replotted on an enlarged scale.

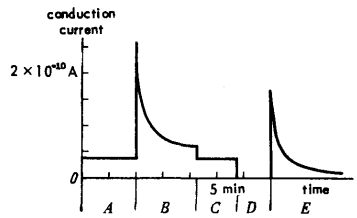


Fig. 4. Variation of the conduction current through a specimen of n-heptane under irradiation (sections *A* and *C*), combined irradiation and illumination (section *B*), and illumination of an irradiated sample (section *E*). Dose rate 0.12 Mrad min^{-1}.[47]

influence of radiation and behaved as traps for current carriers, and to calculate the concentration of traps present in the specimen before irradiation. The concentration was found[45] to be 10^{19}–10^{20} cm^{-3}. The suggestion that free radicals in saturated hydrocarbons can act as traps for charges at low temperatures was first put forward by Tal'roze[46].

The reported photoconductivity[10,35,47] of saturated hydrocarbons during and after irradiation is further confirmation of the capture and accumulation of electrons in hydrocarbons during irradiation. Photoconductivity has been observed also in irradiated aromatic hydrocarbons[48]. Fig. 4 shows typical plots of the current through a specimen of frozen n-heptane, recorded during irradiation with fast electrons and/or visible light[47]. The conductivity peak observed upon exposure to light is due to the emission of current carriers from traps, and the decay is due to the destruction of traps. The amplitude of the photoconductivity peak is proportional to the concentration of trapped current carriers, and can be used as a measure of this concentration. By measuring the amplitude of the photoconductivity as a function of dose Yakovlev and Frankevich[10] were able to monitor the filling of the traps during irradiation and to estimate the limiting concentration of filled traps. This was found to be 10^{17}–10^{18} cm^{-3}, that is, a small fraction of the total concentration of traps.

The low degree of filling implies a mechanism of annihilation of the traps other than thermal excitation, whose probability at a temperature of -196°C is extremely small. Such a mechanism is operative in schemes *II* and *III* of Fig. 2: it involves recombination with mobile "holes"[51] and excitation of trapped current carriers by the resulting energy transfer. It is probable that the positive charges (or "holes") are able to contribute to conduction for a short period following their generation, whilst they remain excited, and become stabilised only after their excitation energy has been dissipated.

The following observations are relevant to a discussion of the factors which cause freezing of the holes. Obviously, the motion of positive charges implies resonance charge transfer between neighbouring molecules. The positive charges in saturated hydrocarbons are localised at individual $-CH_2-$ groups. The ionisation potential of a $-CH_2-$ group depends on the position of the group within the molecule, being lower for central groups and increasing towards the ends of the molecule. This is because the positive charge polarises the molecule, and the gain in polarisation energy is greatest when the charge is located centrally. The existence of a difference in ionisation potential, which can be as large as 0.3 eV for 2–3 $-CH_2-$ units, makes the movement of holes very slow at low temperature. Charge transfer occurs by an electronic mechanism, and does not involve, in keeping with the Franck–Condon principle, any change in the relative positions of atoms. However, the mean interatomic distances in an ion and in a neutral molecule are different, and vibrational excitation of the ions and molecules is needed for charge transfer: this can significantly retard the charge transfer at low temperatures.

Furthermore, positive charges can fall into traps which they "dig" for themselves by undergoing ion–molecule reactions. Thus, the positive charge formed by the exothermic reaction

$$\begin{array}{l} -CH_2-CH_2^+-CH_2- \\ -CH_2-CH_3-CH_2- \end{array} \longrightarrow \begin{array}{l} -CH_2-CH_3^+-CH_2- \\ -CH_2-\dot{C}H-CH_2- \end{array}$$

on a $-CH_3^+-$ group cannot even move to one of the neighbouring $-CH_2-$ groups, because this would involve overcoming a potential energy barrier†.

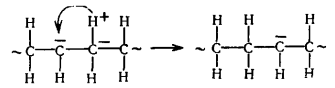
One possible cause of the low degree of filling of the traps by electrons could be the excitation of the electrons by the energy of the radiation, a term which includes here all forms of energy present in the irradiated material: non-equilibrium vibrational excitation energy, electronic excitation energy, light, and slow electrons (sometimes called "subelectrons"[49,50]). The fractional filling of the traps by electrons, n_-/N_t, is a very sensitive function of the probability of excitation of a trapped electron. For scheme *III* of Fig. 2 it can be shown that

$$\frac{n_-}{N_t} = \sqrt{\alpha}\Big/\sqrt{\frac{\sigma_c}{\sigma_r}\cdot\sqrt{\gamma}},$$

where α is the relative probability of excitation of a valence electron and of an electron captured in a trap, γ the number of traps expressed as a fraction of the total number of molecules, σ_r the cross-section for the recombination of an electron with a positive ion, and σ_c the cross-section for the capture of an electron by a neutral trap.

Calculation shows that even for $\alpha = 10^{-2}$ the fraction of filled traps is $n_-/N_t = 10^{-2}$, in qualitative agreement with the experimental value.

The concentration of all charges which accumulate in various saturated hydrocarbons has been measured[52] by studying the relaxation polarisation which appears after irradiation of the materials at low temperature (-196°C) with a 10–50 Mrad dose: the value obtained was 10^{19} cm^{-3}. Since the relaxation time of the charges was found to increase monotonically with molecular chain length in the hydrocarbon series (C_6–C_{12}, C_{25}, polyethylene) examined, a model was put forward according to which a charge localised on a deep trap (a free radical) can move as a result of proton transfer:



This process has a relatively low activation energy for intramolecular transitions (estimated[52] to be 0.06 eV), and accounts for the comparatively high mobility of positive charges within the limited potential wells associated with

† It should be noted that movement of the charge within the molecule may still be possible owing to resonance proton transfer.

the molecules. Limited motion of this type manifests itself as relaxation polarisation, observed when irradiated hydrocarbons are allowed to warm up. Molecular transitions giving rise to electrical conduction in the sample after irradiation and heating appear to need a higher activation energy (0.6 eV, as estimated from the initial portion of the thermally stimulated current curves).

5. Determination of the Electron Yield in the Solid Phase

Gemant[53] made a direct estimate of the yield of electrons in solid hydrocarbons, by measuring the time constant T for the establishment of electrical conduction in a paraffin film enclosed between two electrodes and irradiated with β particles. The intensity of irradiation was low, and the lifetime of the charges was determined only by the transit time of the current carriers between the electrodes. Under these conditions the radiation yield of charges taking part in electrical conduction is 0.036 for 100 eV, and their mobility is 5×10^{-8} cm^2 V^{-1} s^{-1}. This value is fairly close to the yield of free charges measured in liquid n-hexane[11]. The low mobility is evidence that either the current carriers move "from trap to trap" or the mobile species are ions.

Frankevich and Balabanov[54] attempted to measure the yield of all charges formed during bombardment of a paraffin with electrons. A thin film of paraffin, enclosed between two electrodes, was irradiated by a short pulse of electrons of energy 3–5 keV, and the current pulse in the specimen circuit due to the motion of the resulting charges in an electric field was measured. Immediately after their generation all charges act as current carriers and contribute to the conduction current. If a high concentration of traps is present in the specimen some of these charges are captured by traps, and charge recombination (which "confiscates" the contribution of the charges to the conductivity) takes place with a time constant equal to the lifetime in the traps. Measurements showed[54] that a large proportion of the electrons actually return to "their own" ions, and that their trapped time for the C_{25} paraffin at room temperature amounts to tens of seconds. Measurements of the conductivity pulse give $G\mu\tau = 2.6 \times 10^{-12}$ cm^2 V^{-1}. Hence, and from the maximum diffusion length of an electron in the electric field — which for an electron which does not become free cannot exceed $r = \sqrt{e/\epsilon E}$, where E is the external field strength and ϵ the dielectric constant — the yield of electrons captured by traps upon irradiation could be calculated, and the value obtained was $G > 1$. These results also showed that each electron, on the average, migrates more than 30 Å from "its own" ion if the total radiation yield of electrons is taken to be $G = 3$.

III. METHODS OF DETERMINING IONS IN CONDENSED HYDROCARBONS WHICH DO NOT DEPEND ON THE ELECTRICAL PROPERTIES OF THE IONS

In addition to their electric charge, which is their most fundamental property, ions have a number of other properties, less specific but nonetheless characteristic, which can be used to identify the ionised states formed in an organic compound by the action of radiation. The following properties have been used to detect ions: the magnetic moment (for paramagnetic ions), the absorption spectrum, and the light emitted by the recombination of ions with electrons.

Many workers have observed a light-sensitive line, which disappears on exposure to visible light, in the ESR spectrum of alcohols[55,56], polyethylene, paraffin, and rubbers[57] irradiated at low temperatures. Sensitivity to light in the visible region suggests weak bonding of the electron, and justifies the conclusion that this ESR line is due to electrons held in traps of some kind. The presence of trapped electrons is confirmed by the development of colour on irradiation and by the thermoluminescence of hydrocarbons irradiated at low temperature and allowed to warm up[55,58-60]. Heating the specimens causes luminescence and at the same time bleaches them. It has been shown[61,62] that the luminescence appears at temperatures corresponding to phase transitions in the irradiated material, and is associated with faster diffusion of the charged particles. The luminescence centres are usually provided by some impurity present in the material which is excited by acquiring the energy evolved by the recombination of charges. The recombination does not involve emission of the electrons from the traps: this follows from the observation that the depth of the traps as deduced from the photoluminescence excitation spectrum in irradiated hydrocarbons (n-hexane, nonane, 2,4-dimethylundecane, tetradecane, cyclohexane, dicyclohexyl-4-decane, polyethylene)[63] is fairly large (2–3 eV) and does not agree with the depth measured by the appearance temperature of the thermoluminescence peak. The photoluminescence excitation spectra of irradiated hydrocarbons have been found[63] to depend on the total dose of radiation. At high doses (> 10 Mrad) the spectrum is displaced towards the short-wave region, pointing to the appearance of new, deep traps on irradiation. These traps are, very probably, free radicals[45].

Many workers have studied the appearance of ions in two-component systems (solid solutions), because these systems offer the possibility of identifying certain ions either by their absorption spectra or by their ESR spectra. Therefore, additives able to give rise to such ions offer a means of monitoring their formation and accumulation under irradiation.

It should be noted that the formation of ions of the second component in two-component systems can occur by direct ionisation, but also as a result of charge transfer, excitation transfer, or ionisation by subelectrons, that is, electrons whose energy is less than the ionisation potential of the molecules of the major component. At low additive concentrations we can ignore direct ionisation, but it is not always possible to choose unequivocally among the other possible processes.

Bagdasar'yan and his coworkers[64-66] have studied the formation of positive ions of aromatic amines in matrices of methylcyclohexane, isopentane, and poly(methyl methacrylate). Samples were exposed to γ-radiation at -196°C. The ions of aromatic amines were identified by their known absorption spectra. The yield of positive ions of the amines in a hydrocarbon glass was 0.16 (at an impurity concentration of 0.005 M) on the basis of the energy absorbed by the whole of the sample; in poly(methyl methacrylate) G(ions) = 3 at an impurity concentration of 0.1 M. The limiting concentration of ions was 10^{-5} and 10^{-3} M in the two experiments respectively, and did not increase when the additive concentration was increased. The authors suggest that the amine ions are formed by the capture of positive charges (initially generated in the matrix) by solute molecules. However, they do not exclude the possibility of ionisation of the amines by excitation energy gained from the matrix[67].

The formation of positive ions of *NN*-dimethyl-*p*-phenylenediamine (DMPD) was studied spectroscopically by introducing the amine into various matrices[68] and than irradiating with γ-rays at -196°C. A high yield ($G \simeq 2$) of DMPD ions was obtained in non-polar media, but in polar media (alcohols) the yield was much lower under otherwise identical conditions. Addition of an electron-acceptor impurity to the matrix as well as the amine raised the yield of DMPD cations to 4 in non-polar media and by a small amount in polar media. These results were interpreted in terms of the capture by amine molecules of positive charges formed by ionisation of the matrix. The small yield of cations in polar media is tentatively ascribed to an ion–molecule reaction observed in the gas phase[69], of the type

$$C_2H_5OH^+ + C_2H_5OH \longrightarrow C_2H_5OH_2^+ + C_2H_5O.$$

leading to positive charge "capture". The presence of acceptor molecules lowers the mobility of electrons and precludes to some extent their recombination with positive charges.

The formation of negative ions has been observed spectroscopically and by ESR in poly(vinyl chloride) and poly(methylmethacrylate) containing electron-acceptor impurities (quinones, polycyclic aromatic compounds, etc.)[70]. These were irradiated with γ-quanta at -196°C. The concentration of additives was between 0.03 and 0.6 mole %. Under these conditions the yield of anions, calculated on the basis of the energy absorbed by the acceptor molecules in the system, amounted to 100–1000. This is evidence for energy transfer from the matrix to the impurity. The authors suggest that the impurity directly captures an electron which would otherwise by captured by a polymer molecule. They point out that the retrapping of an electron by an impurity completely suppresses the formation of conjugated bonds and the appearance of colour in poly(vinyl chloride) upon irradiation.

Guarino and coworkers[71,72] have reported a systematic investigation of the formation of negative ions in hydrocarbon matrices. Naphthalene or biphenyl impurities were introduced into a matrix of tetrahydro-2-methylfuran (THMF). The absorption spectra and the extinction coefficients of the negative ions produced from these molecules are known, since the ions can be prepared chemically by reduction with alkali metals (with formation, for naphthalene, of $Na^+C_{10}H_8^-$). The samples were irradiated with γ-rays at -196°C. In a glassy matrix of THMF containing naphthalene the limiting yield of $C_{10}H_8^-$ anions was found to be 2.6; with biphenyl as the impurity the yield (of $C_{12}H_{10}^-$ ions) was 3.2. In hydrocarbon glasses containing the same impurities the anion yield was 1.1 and 1.7 respectively, whilst in an ethanol matrix the yield of anions was 2.94. When the impurity concentration was of the order of 0.05 mole %, the yield was close to unity in all media. Evidently, as in any other two-component medium, the retrapping of an electron ejected from a molecule of the solvent is not the only possible mechanism of formation of ions of the minority component. Ionisation by excitation transfer or by subelectrons is also possible. Further experiments were needed to substantiate the authors' contention that the measured electron yields applied to free and thermally generated electrons formed by the ionisation of the substrate. Thus, it was found that an absorption band which can be bleached by light is formed in THMF even in the absence of added impurities. When the absorption band of the matrix was bleached using a specimen which had been irradiated in the presence of impurities it was found that the concentration of impurity ions rose. This points to the transfer of electrons, initially stabilised in the matrix, to the impurity molecules. The observed competition between two different impurities added to THMF[72–74] is further evidence that the impurity molecules act only as acceptors of electrons generated in the matrix. Thus, if THMF contains only naphthalene (at a concentration of 0.11 mole %) the yield of $C_{10}H_8^-$ ions is 1.63, but the value is lowered when competing substances are added. The decrease caused by various "secondary" impurities is a relative measure of their electron-capturing efficiency. The formation of anions by electron retrapping must involve the scheme

$$M \rightarrow M^+ + e$$
$$X + e \rightarrow X^-$$
$$Y + e \rightarrow Y^-,$$

where M is a molecule of the major constituent, and X and Y are impurity molecules.

If X^- is identified with the $C_{10}H_8^-$ anions, whose concentration can be measured, the measured yield G_{X^-} is related to the impurity concentrations C_X and C_Y as follows:

$$\frac{1}{G_{X^-}} = \frac{1}{G_e^0} + \frac{\sigma_Y}{\sigma_X}\frac{C_Y}{C_X}\cdot\frac{1}{G_e^0}.$$

This formula is correct if the $C_{10}H_8$ molecules capture all the electrons in the absence of a "second" impurity: G_{X^-} is equal to G_e^0 when $C_Y = 0$. Table 3 lists some relative capture efficiencies (σ_Y/σ_X) for electrons, measured experimentally[72] with different Y molecules as the "second" impurity.

The series of relative electron-trapping efficiencies obtained is consistent with the known trapping properties of many of these molecules towards thermal electrons. It was found that the lower the threshold energy in the plot of electron capture cross-section against energy, the more effectively molecules behave in competing for electron capture during radiolysis. The threshold energies for electron capture by HI and HCl molecules are 0 and 0.66 eV respectively; the threshold energies for CCl_4 and $CHCl_3$ are 0.03 and 10 eV. In keeping with these figures, we see from Table 3 that HI molecules are mo efficient electron acceptors than HCl; CCl_4 molecules are much more effective than CH_3Cl. Moreover, it was found that the relative electron trapping efficiency of these molecules increases in the same order as their polarographic half-wave potential.

TABLE 3.

Y	CH_3Cl	C_2H_5OH	C_6H_6	BF_3	CH_3CCCH_3	H_2O	$CH_2(CH)_2CH_2$	NO	N_2O
σ_Y/σ_X	0	0	0	1	1	1	2	3	4

Y	C_6H_5Br	$CH_3CHClCH_3$	HCl	C_2H_5I	O_2	$C_6H_5CH_2COCl$	HI	CH_3I
σ_Y/σ_X	5	5	5	6	9	10	11	12

Y	$CHCl_3$	$CH_3CO_2CH_2C_6H_5$	CCl_4	$CHBr_3$	C_6H_5CHO	SO_2	CBr_4	I_2
σ_Y/σ_X	15	17	20	20	22	23	25	37*

* $\sigma_{I_2} = 3.2 \times 10^{-15}$ cm^2.

Similar results were obtained[74] by adding biphenyl and various benzene derivatives to a THMF matrix. The measured relative electron trapping efficiencies (σ_Y/σ_X) are set out in Table 4 (where X = biphenyl).

The results of these investigations[71-74] provide convincing proof that the yield of electrons which can be trapped by various impurities is high in hydrocarbons, and corresponds approximately to the yield of electrons in the gas phase.

By using flash irradiation, which can generate a high concentration of ions, it has been possible to estimate the ions in the liquid phase. Thus, an absorption spectrum has been observed[75] in the region of 2970 Å after flash radiolysis of liquid 2-methylpropene. Trimethylcarbonium ions are known to absorb in this region. The lifetime of the ions was 0.05 s at -15°C. These experiments are similar to those which revealed the presence of solvated electrons in water during irradiation[24].

The overall conclusion from all the data presented in Sections II and III is that the work published so far provides sufficient grounds for the confident assertion that electrons and ions are formed and have an appreciable existence in a condensed phase.

The lifetime of electrons and ions before they mutually recombine is such, even for recombination in pairs, that processes involving the capture of electrons by traps, by specially added acceptor molecules, and therefore also by electron-acceptor radiolysis products, can compete with the electron–ion recombination process. We may conclude from the results discussed above that the following are the most important processes involving charged particles in an organic material:

ionisation	$M + e \rightarrow M^+ + 2e$
recombination of an electron with "its own" ion	$M^+ + e \rightarrow M^*$
electron capture by impurities competing with recombination	$T + e \rightarrow T^-$
recombination of T^- ions (or e^-) with M^+	$T^- + M^+ \rightarrow$ products

If the time during which M^+ ions, and also X^- and T^- ions, can exist is long enough for these ions to take part in ion–molecule reactions, the products of these reactions will take part in the recombination process.

In the liquid phase the time of separate existence of electrons and ions is determined by the time which they take to diffuse towards each other from distances not exceeding r_c but greater than 30 Å (see p. 493). If we assume a mobility for electrons in n-hexane[17] of 10^{-3} cm^2 V^{-1} s^{-1}, a typical lifetime of charges in an organic liquid works out to[76]:

$$\tau = \frac{\varepsilon}{3\mu e^2} r_c^3 \simeq 10^{-7}\ \text{s}.$$

For free electrons the lifetime is very much greater, and depends on the total concentration of ions. However, the yield of free electrons is no more than 3–5% of the total, as was pointed out above.

The existence of two groups of electrons upon irradiation, with widely different lifetimes for recombination, was stressed by Williams[76] in his study of liquid cyclohexane. He showed that addition of a low concentration of ND_3 to cyclohexane leads to the formation of HD molecules, the yield being independent of the impurity concentration over the range 10^{-4}–10^{-2} M and increasing with $\sqrt{[ND_3]}$ at higher concentrations. Since the formation of HD was shown to occur by the process

$$ND_3 + C_6H_{12}^+ \longrightarrow ND_3H^+ + C_6H_{11},$$
$$ND_3H^+ + e \longrightarrow NH_3 + D \text{ (and also } NH_2D + H)$$
$$D + C_6H_{12} \longrightarrow HD + C_6H_{11},$$

it follows that the measured yield of HD is a measure of the number of charges which can be captured by ND_3 (to give ND_3H^+). The lack of dependence of the yield of HD upon the concentration of additive is evidence that the lifetime of at least some of the charges is very long: this fraction of the charges is estimated to be formed with a yield of 0.08, in good agreement with the yield of free carriers[11,15]. The lifetime of the charges formed in very much greater yield was estimated to be 10^{-7} s.

In a solid phase, and particularly at low temperatures, the lifetime can be quite high, and it is always higher than in the liquid phase.

TABLE 4.

Impurity	Biphenyl	Triphenylene	Phenanthrene	o-Terphenyl	Cycloheptatriene	Pyrene
σ_Y/σ_X	1	1.04	1.22	1.40	1.94	1.95

Impurity	1,2-Benzanthracene	Triphenylethylene	Tetraphenylethylene	Anthracene	Hexamethylbenzene
σ_Y/σ_X	2.70	2.60	2.76	2.76	2.80

IV. REACTIONS OF CHARGED PARTICLES IN A CONDENSED PHASE

1. Main Types of Reaction

The ions and electrons formed in a condensed phase are active particles, free to take part in many chemical reactions. The high activity of charged particles has been demonstrated in many investigations of ion–molecule processes in the gas phase, showing that exothermic or athermic ion–molecule reactions involve a negligibly small activation energy. Since the lifetime of ions in a condensed phase is greatly in excess of the time between collisions (10^{-13} s), it is obviously possible for the ions to take part in various reactions. In consequence, ionised products of these reactions can often take part in the recombination process instead of the molecules initially ionised.

Processes involving charged particles during their lifetime can have a profound effect on the chemical action of radiation. Among these processes, the following are the most important.

Processes with the participation of positive charges: unimolecular decomposition; positive charge transfer to molecules of lower ionisation potential than the molecules of the substrate; ion–molecule reactions.

Processes with the participation of electrons: electron transfer to molecules of higher electron affinity than the molecules of the substrate or to traps of structural origin;

unimolecular decomposition of a molecule containing a trapped electron; ion–molecule reactions.

The chain of transformations involving positive and negative charges ends when the charges recombine.

In most instances, workers can critically assess various processes in a condensed phase by referring to the considerable fund of experimental data on the formation of stable radiolysis products. In a condensed phase it is not possible as a rule to examine in detail any particular elementary reaction, including reactions between ions and molecules, by observing the initial particles and their transformation products, as can be done in the gas phase. Therefore, experimental results can often be "satisfactorily" explained by different mechanisms. In these circumstances, the most valuable investigations are those offering some direct evidence that the primary particles leading to the observed product by a clearly defined reaction were ions.

The main criterion of whether any given reaction proceeds with the participation of charged particles is the energy of the reaction. One usually refers to the published heats of the corresponding reactions in the gas phase. This can be justified for processes not accompanied by the disappearance of charges, because a condensed phase lowers the ionisation potential of molecules by the polarising effect of the medium and ion solvation but has no effect on the "neutral" properties of molecules. The lowering of the ionisation potential on changing from the gas phase to a condensed phase drastically decreases the exothermicity of ion recombination processes. Processes involving ions and electrons will be examined in detail in the following subsections.

2. Dissociation of Ions

A positive ion, usually in an excited state when first formed, very quickly (in 10^{-8}–10^{-13} s) loses its excitation energy by collisions with the surrounding molecules.

Dissociation of an excited ion can occur only if the resulting fragment is able to escape from its partner by diffusion: otherwise, the cage effect[77] causes recombination of the ion. It follows that, in practice, the only possible products of dissociative ionisation in a condensed phase are an H atom or a proton. An ion can dissociate from its ground state without any restriction as to the residues only if energy is evolved[78]. A thermochemical calculation shows[79] that dissociation is energetically favourable when, for example, an alkene ion is formed from a saturated hydrocarbon:

$$C_6H_{14}^+ \longrightarrow \begin{cases} \longrightarrow \textit{trans}\text{-}2\text{-}C_6H_{12}^+ + H_2\ (+4\ \text{kcal mole}^{-1}) \\ \longrightarrow \textit{trans}\text{-}3\text{-}C_6H_{12}^+ + H_2\ (+5\ \text{kcal mole}^{-1}). \end{cases}$$

The attachment of an electron to a molecule can also lead to dissociation in apparent contradiction to the cage effect: dissociation of this type occurs if the electron affinity of the resulting fragment is greater than the bond dissociation energy. Dissociation processes of the type $RX + e \rightarrow R + X^-$, well known in mass-spectrometric investigations, are found to be exothermic and to have a threshold at thermal electron energies. A similar process has been observed[80] in solid hydrocarbons containing small amounts of $C_6H_5CH_2Cl$. When an electron, freed from a trap by the action of light in irradiated methyltetrahydrofuran, becomes attached to a $C_6H_5CH_2Cl$ molecule, the formation of $C_6H_5\dot{C}H_2$ radicals can be observed in the solid phase. Similar results have been obtained in studies of other additives of the type RX (where $R = C_6H_5\dot{C}H_2$; $X = CH_3COO$, CH_3O). The efficiency of various additives towards electron capture depends critically on the appearance potential of the X^- ions in the dissociation process, and varies in the same sense as this potential.

3. Charge Transfer

The interaction between positive charges and their surrounding molecules can lead to two types of effect. The first, charge transfer, cannot lead to chemical changes in a homogeneous medium; its only effect is to facilitate the diffusional transfer of charges. In two-component or multicomponent media charge transfer enables the positive charge to become localised on the molecules of lowest ionisation potential. The energy of the ionisation process, given out when a positive and a negative charge recombine, is evolved mainly at these particular molecules[81,82]. This may be the cause of deviations from the so-called law of radiation-chemical additivity (sometimes also termed the "law of mixtures"). The deviation consists in the following: the fraction of the total yield of products contributed by the decomposition of these "acceptors" of energy is higher than expected by considering only what fraction of the energy has been directly imparted by the radiation to the molecules of low ionisation potential. If the charge transfer process is sufficiently effective, the molecules of low ionisation potential will behave as protective additives which concentrate on themselves the main effect of the radiation and thus protect the surrounding medium. According to their chemical stability, these impurities can decompose or they can scatter the energy, the protection being of the "sacrificial" or the "sponge" type in the two cases respectively[83]. It should be noted that charge transfer effects can play an essential role also in the radiolysis of one-component systems, because new molecules are formed in the course of radiolysis and these can concentrate on themselves an increasing fraction of the radiation energy if their ionisation potential is lower than that of the molecules of the major constituent of the medium.

The deviations from the law of mixtures reported so far are very numerous[84,85]. They can be explained, in principle, by the most diverse mechanisms of energy transfer, charge transfer being but one of many possibilities. Hardwick[86] has pointed out that the departures from the law of mixtures in two-component solutions of aliphatic hydrocarbons are always in the sense of energy transfer to the molecules of lower ionisation potential. This conclusion was reached from a study of the yield of hydrogen, which was a product of the decomposition of each of the components of the mixture (n-hexane–neohexane, n-hexane–2,3-methylbutane, and many others). The law of mixtures predicted a hydrogen yield varying linearly with the composition of the mixture, but in practice, owing to energy transfer, this relationship was not observed.

Molecules which behave as charge acceptors, that is, those of lower ionisation potential, can also act as acceptors of excitation energy, because their electronic excitation levels are usually lower. This phenomenon often militates against a definite clarification of the mechanism of energy transfer.

Many workers have examined, spectroscopically or by ESR methods, the state of impurities added to an irradiated substance which have a protective action on the specimen. It was found that the molecules of the additive become ionised. Thus, when poly(methyl methacrylate) is protected from degradation by adding aromatic amines, positive amine ions are detected spectroscopically[64]. The radiation yield of these ions is equal to the fall in the yield of the chain-breaking process in the polymer. Addition of electron-acceptor impurities (quinones, polycyclic aromatic compounds) to poly(vinyl chloride) (PVC) suppresses[79] the formation of conjugated bonds in the PVC and greatly lowers the yield of HCl. This, evidently, results from the transfer of a charge (an electron) to the acceptor. The spectrum of the negative ions of the impurity has been examined by ESR. Studies illustrating the transfer of positive[65-68] and negative[56,71-74] charges to molecules of impurities specially added to hydrocarbon substrates at low temperatures have already been considered in the previous subsections.

4. Ion–Molecule Processes

Ion–molecule reactions are the second type of process in which ions can take part. Two basic types of reaction have been identified in hydrocarbons in the gas phase: reactions involving the transfer of heavy particles such as an H atom, a proton, or a hydride ion, and reactions leading to the synthesis of a C–C bond[2,4,46]:

$$R'H + R''H^+ \longrightarrow R'H_2^+ + R'' \quad \text{(proton transfer)},$$

$$R'H + R''H^+ \longrightarrow R' + R''H_2^+ \quad \text{(H atom transfer)},$$

$$R'^+ + R''H \longrightarrow R'H + R''^+ \quad (H^- \text{ ion transfer}),$$

$$R'H^+ + R''H \longrightarrow R'R''^+ + H_2 \quad \text{(synthesis of a C–C bond)}.$$

In a condensed phase these reactions can act as a source of free radicals and determine the formation of cross-links. The small temperature dependence of the radiation yield of cross-linking in saturated hydrocarbons and the possibility of inhibiting cross-linking by adding suitable impurities[87,88] have been interpreted as an indication that ion–molecule reactions are responsible for the formation of cross-linked structures. Various reactions have been suggested:

$$(1)\ RH + RH^+ \longrightarrow RR + H_2^+ \ [89]$$

$$(2)\ RH + RH^+ \longrightarrow RR^+ + H_2 \ [90]$$

$$(3)\ RH^+ + R \longrightarrow RR + H^+ \ [91]$$

$$(4)\ \begin{cases} RH + RH^+ \longrightarrow RH_2^+ + \dot{R} \\ RH_2^+ + e^- \longrightarrow H_2 + \dot{R} \end{cases} \longrightarrow RR \ [92]$$

Thermochemical calculations give the heats of these reactions as -4.72, 0, -2.50, and 9 eV respectively, so that at least two of them, (2) and (4), could control the formation of cross-linking. Available data do not allow an easy choice between these two alternatives, because their occurrence in a condensed phase has not been directly reported. The distribution of isomers of the C_{12} dimer formed during the low-temperature radiolysis of n-hexane, investigated by Kevan and Libby[92], can be satisfactorily explained on the basis of reactions (2) and (4).

The positive charge, having taken part in an exothermic ion–molecule reaction, is found in a deep trap, where it loses its activity and takes no further part in chemical processes until it finally recombines. However, if the reaction involving the positive ion enables the ion to retain its original activity, the same ion can, of course, take part in a whole series of ion–molecule processes. The most important of these is ionic radiation polymerisation, proposed in order to explain the large yield of polymer in irradiated 2-methylpropene[93,94]. The characteristic features of ionic polymerisation are: a weak temperature dependence of the rate of polymerisation (even a negative temperature coefficient being reported[96]), and a constant molecular weight of the resulting polymer over a wide range of radiation intensities, due to the fact that the lifetime of the chain carriers is independent of the intensity of irradiation. These facts cannot be explained by applying the ideas of the free-radical mechanism of polymerisation, but they fit quite satisfactorily into the conceptual framework of ionic processes[93-95].

The ion R^+, leading to polymerisation, can be formed either directly in the primary ionisation event or as a result of an ion–molecule reaction:

$$M \rightsquigarrow R^+;$$

the chain propagation reactions being

$$R^+ + M \longrightarrow RM^+$$

$$RM_n^+ + M \longrightarrow RM_{n+1}^+.$$

The chain-breaking reactions can take the form of charge transfer

$$RM_n^+ + M \longrightarrow RM_n + M^+$$

or recombination

$$RM_n^+ + e \rightarrow RM_n.$$

The important role of ions in the polymerisation of 2-methylpropene has been demonstrated by many direct experiments. Thus, it has been shown[94,97,98] that the appearance of free radicals in liquid 2-methylpropene at -78°C does not lead to polymer formation. However, the introduction of positive ions formed in the gas phase into liquid 2-methylpropene causes it to polymerise[99]. The application of an electric field strength of 10^4 V cm^{-1} to 2-methylpropene during irradiation raises the yield of polymer[100] by a factor of 3. This has been ascribed[100] to the greater yield, in an electric field, of free charges which do not recombine with "their own" ions. The reaction is probably initiated by a proton, formed by the primary ionisation act:

$$(CH_3)_2C{=}CH_2 + H^+ \longrightarrow (CH_3)_2CHCH_2^+.$$

The $C_4H_9^+$ ion propagates the polymerisation chain. We know also that the $C_4H_9^+$ ion is formed in gas-phase ion–molecule reactions when 2-methylpropene is ionised.

The only real proof of the role of ion–molecule reactions in the polymerisation of liquid alkenes was obtained[103,104] in a study of the polymerisation of a mixture of C_2H_4 and C_2D_4. By plotting the mass spectrum of the products of radiation polymerisation (up to C_{18}) it was shown that the number of D atoms in the polymer molecules is invariably a multiple of four. This is evidence that the molecular ions $C_2D_4^+$ are taking part in the polymerisation reaction. The reaction itself is apparently of the form

$$C_nH_{2n}^+ + C_2H_4 \rightarrow C_{n+2}H_{2n+4}^+$$

where n = 2, 4, 6, ... The polymerisation chain is broken by the recombination of the ion with an electron. Ionic polymerisation has been recently demonstrated mass-spectrometrically in ethylene in the gas phase, under high pressures[105].

Still further proof of the role of ions in the polymerisation of unsaturated hydrocarbons is the influence of charge-acceptor impurities on the yield of polymers. Thus, addition of ammonia to liquid cyclopentadiene strongly inhibits polymer formation under irradiation [106]. Ammonia undergoes an ion-molecule reaction in pentadiene with proton transfer, giving rise to an NDH_4^+ ion which breaks the polymerisation chain. By measuring the degree of polymerisation as a function of dose in the presence of various concentrations of added ND_3 it was possible to estimate the mean growth time of the chain, equal to the lifetime of the ion, which turned out to be 10^{-3} s for the formation of chains 10^3–10^5 monomer units long. The long lifetime of the ions suggests that only free ions which have escaped recombination can be involved [107]. Of course, shorter-lived ions which have failed to escape from the coulombic interaction with "their own" electron can participate in the formation of shorter chains during polymerisation.

5. Recombination of Ions

The last reaction in which the chemical activity of ions can be utilised is ion recombination. The importance of this process in radiation chemistry was realised from the very earliest radiation-chemical investigations [108,109]. The special features of recombination processes, particularly in the gas phase, have been discussed on many occasions [81,82,110,111]. The recombination of charges results in considerable excitation of one or two molecules, whose ions take part in the process. This excitation can lead to various chemical reactions, such as dissociation or molecular rearrangement, formation of double bonds or cross-links, and so on. The energy evolved in the recombination process depends on the nature of the recombining particles. It is greatest, and equal to the ionisation potential I_M of the molecules, for recombination in the gas phase ($M^+ + e^- \rightarrow M^*$), but it becomes very much less in a condensed phase, particularly when the electron recombining with the positive ion is bound in an electronegative molecule. It should be noted that the energy evolved in recombination in a condensed phase depends essentially on the mode of dissipation of the kinetic energy of the charged particles approaching one another. Thus, if an electron or negative ion, having been captured by the sphere of action of the coulombic field of an ion of the opposite sign, begins to drift towards that ion and move in what is effectively a "viscous" medium, then the energy evolved during the recombination will obviously be

$$E = I_M - \left[\frac{e^2}{\epsilon r} + Q\right],$$

where Q is the electron affinity of the molecule on which the electron is localised before recombination; r is the distance between the charges corresponding to electron transfer rather than drift of the charges in a "viscous" medium. The sum $(e^2/\epsilon r) + Q$ can have quite large values: thus, for $r = 3$ Å and $\epsilon = 2$, $e^2/\epsilon r = 2.5$ eV. The variation of the energy evolved in the recombination with the nature of the negative ion can account for the protective action of various electron-acceptor impurities during radiolysis [83]. If the quantity E is decreased below the level required for dissociation of the molecule, protection becomes possible. This interpretation has been used, for example, in studies of the inhibition by N_2O impurities of the yield of hydrogen in the liquid-phase hydrolysis of saturated hydrocarbons [112]. Since it is known that after capturing an electron N_2O dissociates to form N_2 and O^-, the lower hydrogen yield in the presence of N_2O may be ascribed to the occurrence of the reaction $M^+ + O^-$, which does not produce hydrogen, instead of the reaction $M^+ + e^- \rightarrow H_2$, characteristic of the pure alkane.

Very few papers have dealt with direct experimental studies of the chemical effects of recombination, even in the gas phase [113,114].

The first attempt to identify the products of the recombination process in a condensed phase was made in this laboratory [115,116], relying on the fact that ions and electrons can be made to accumulate when radiolysis is carried out at low temperatures. Recombination can be induced by freeing the charges with light after irradiation, and this is a method for carrying out the ionic reaction under controlled conditions. The effect of visible light on n-heptane irradiated at -196°C is to produce a measurable evolution of hydrogen [115,116], which cannot be explained by assuming that the hydrogen has accumulated in the specimen during irradiation and is freed by the heating effect of the beam of light. We were led to conclude that the hydrogen is formed as molecules in processes such as $M^+ + e^- \rightarrow H_2$ + + double bond, or $M^+ + e^- M \rightarrow H_2$ + cross-linkage.

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The papers discussed in the present review justify the conclusion that the part played by ionised states in radiolysis should not be underestimated. The long lifetimes of ions and electrons in condensed phases allow them to take part in many processes leading to chemical changes in the material.

We are only just beginning to explain the role of ions in various chemical systems under conditions of radiolysis in a condensed phase. Further developments in this field will no doubt advance the state of the art from a rational application of ideas concerning ionic reactions in condensed phases during radiolysis to a general application of these ideas to the interpretation of radiation-chemical processes.

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THE SURFACE TENSION OF MOLTEN SALTS

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I. INTRODUCTION

Molten salts and their mixtures in recent years have been finding ever-increasing application in industry as high-temperature liquids, lubricants, heat-carriers, fluxes, etc. The importance which is being attached to the study of both the bulk and the surface properties of molten salts is thus obvious. Moreover, the study of the physicochemical characteristics of salt melts is a necessary prerequisite for the investigation of the nature of the liquid state and the development of a general theory of liquids.

In view of the vast amount of accumulated information on the physicochemical properties of molten salts in recently published monographs and reviews[1-4] it was impossible to give sufficient attention to each property, including the surface tension of the salts. The increasing interest in experimental data on the surface tension of salts and the non-existence of sufficiently detailed reviews in this field suggest that a review of this type will be opportune and useful.

Before discussing published data on the surface tension of melts, we would point out that we have tried to cover, as completely as possible, papers describing the experimental study of the surface tension of salts and their mixtures; as far as the surface tension of oxide systems is concerned, we have restricted ourselves in the present review to a few papers containing data on the surface tension of the simplest compounds formed in these systems.

II. REVIEW OF EXPERIMENTAL WORK ON THE SURFACE TENSION OF MOLTEN SALTS AND THEIR MIXTURES

The surface tension (σ) of molten salts appears to have been measured for the first time in 1869 by Quinke[5], who used the stationary-drop and drop-weight methods[6-8] to find the capillary constants of melts formed by a number of salts of the alkali and alkaline earth metals. Experimentally, these measurements were unreliable. For example, the temperature of the melts was indefinite, a considerable temperature gradient was unavoidable, and during the measurements there was a danger of decomposition of the melts and contamination from the flame of the heater.

These unsatisfactory features of the determination of σ are also characteristic of the work of Traube[9] and Motylewski[10], who used the drop-weight method find the capillary constants of a large number of inorganic salts.

Bottomley[11] determined σ for $NaNO_3$ and KNO_3 melts using the capillary-ascent method, for which there is much greater theoretical justification[7].

Lorenz and coworkers[12-14] measured σ for $NaNO_3$, KNO_3, $PbCl_2$, $CdCl_2$, KCl, AgCl, and various KCl + $PbCl_2$ and $CdCl_2$ + $PbCl_2$ mixtures by the capillary-ascent method. Unsatisfactory methodological features of the studies are the possibility of contamination of the melt by corrosion products from the walls of the capillaries and the temperature gradient along the capillary.

Of considerable interest in the study of σ for fused salts is the work of Jaeger[15], which has now become classical. Jaeger was the first to measure σ for salts using the maximum gas-bubble pressure method[7,8,16-18], which is apparently the most reliable and convenient and which has subsequently been widely used. Jaeger developed thoroughly a method for measuring σ by this method in the temperature range from -80° to +1650°, and in the high--temperature range he introduced a number of improvements in technique aimed at preventing contamination of the salts, maintaining constant temperature, increasing the accuracy of the measurement of the temperature and pressure, etc. An unsatisfactory feature of his procedure is that the moment when the end of the capillary comes in contact with the surface of the melt is recorded visually, and this is extremely difficult at high temperatures. Jaeger determined the values of σ for almost 200 organic and 50 inorganic liquids. The latter included the alkali metal halides (with the exception of lithium bromide and iodide), nitrates, and sulphates; sodium and potassium metaborates, metaphosphates, molybdates, and tungstates; lithium metasilicate; potassium dichromate; thallium nitrate; sulphur monochloride; the trichlorides of phorphorus, arsenic, antimony, and bismuth; tribromides of phosphorus, arsenic, and bismuth; and phosphorus triiodide. All the substances studied have negative temperature coefficients $d\sigma/dt$. In some instances the value of $d\sigma/dt$ changes with temperature and the σ polytherms are slightly convex away from the temperature axis.

In a study of the properties of salt melts used as electrolytes in magnesium baths, Zhivov[19,20] used the maximum gas-bubble pressure method to measure σ for pure NaCl, KCl, and $MgCl_2$, the binary NaCl–KCl, NaCl–$MgCl_2$, and KCl–$MgCl_2$ systems, and sections of the ternary NaCl–KCl–$MgCl_2$ system at molar ratios KCl : NaCl = = 1 : 1 and 1 : 3. The 700° isotherms for the binary systems containing $MgCl_2$ showed points of inflection corresponding to equimolar mixtures of the components, and the 800° isotherm for the NaCl–$MgCl_2$ system also showed a maximum corresponding to 86 mole % $MgCl_2$. Zhivov (see Mashovets[21]) also measured σ for molten NaF + AlF_3 mixtures at AlF_3 concentrations up to 50 mole %, and molten NaF + AlF_3 (15 mole % and 33.4% AlF_3) + Al_2O_3 (up to 10 wt. %) and Na_3AlF_6 + Al_2O_3 (up to 17.5 wt. % Al_2O_3) mixtures. Within limits of accuracy of the measurements, the addition of Al_2O_3 does not influence the value of σ for the mixtures.

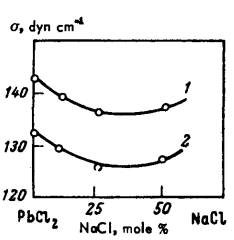

Fig. 1. Surface tension isotherms for the $PbCl_2$–NaCl system[25]: 1) 500°; 2) 600°.

Elchardus[22] used the maximum bubble-pressure method to measure σ for pure Na_3AlF_6 and its mixtures with NaF and AlF_3 (up to 20 wt. % additive). The temperature dependence of σ for Na_3AlF_6 is non-linear, and this is taken as an indication that cryolite dissociates in the molten state.

Jarrat and Prideaux[23] measured σ for melts using Sugden's version[7,24] of the maximum gas-bubble pressure method, using two capillaries; an advantage of this method is that it eliminates the measurement of the depth to which the end of the capillary is immersed in the melt. This method was used to find σ for molten $HgCl_2$ and $HgBr_2$ close to the melting points.

Barzakovskii[25,26] measured σ for the binary NaCl–KCl, $CaCl_2$–NaCl, and NaCl–$BaCl_2$ salt systems throughout the entire concentration range and for the NaCl–$PbCl_2$ system in the range 0–50 mole % NaCl. The isotherms for these systems are linear or slightly convex towards the composition axis; only the 500° and 600° isotherms for the NaCl–$PbCl_2$ system show minima corresponding to 30 mole % NaCl (Fig. 1).

Semenchenko and Shikhobalova[27-30] used the maximum gas-bubble pressure method to study σ for a number of salt melts up to 1100°. As an improvement in technique they introduced a convenient method in which the moment when the end of the capillary came in contact with the melt was recorded by direct electrical contact. The values of σ were measured for Li_2SO_4, LiCl, $NaNO_3$, Na_2SO_4, NaCl, K_2SO_4, KCl, KBr, KI, RbCl, CsCl, $BaCl_2$ and the organic salts CH_3CO_2K and $C_2H_5CO_2K$, and also for mixtures of the binary systems $NaNO_3$–(NaF, NaCl, NaBr, NaI, CH_3CO_2K, and $C_2H_5CO_2K$), Na_2SO_4–(NaCl, NaI, KCl, KBr, and KI), and K_2SO_4–KCl at concentrations of the second component not exceeding 50 mole %, and for mixtures of the systems Li_2SO_4–(NaCl, KCl, RbCl, CsCl, and $BaCl_2$), LiCl–RbCl, and $NaNO_3$–(CH_3CO_2K and $C_2H_5CO_2K$) in the concentration range from 0 to 100%. The isotherms for all the systems are convex towards the composition axis. The isotherms for the Li_2SO_4–$BaCl_2$ system show a deep minimum which was attributed to the formation of the sparingly dissociated barium sulphate (Fig. 2). On the isotherms for the Li_2SO_4–(NaCl, KCl, RbCl, and CsCl) systems, small (1–2 mole %) horizontal sections were distinguished at low concentrations of the second component. The scatter in the experimental points in these ranges is scarcely greater than the error in the determination of σ (1.5–2% according to the authors), so that these isotherms can be regarded as smooth curves. On the basis of the data obtained, it was concluded that small quantities of the additives influence the value of σ and the crystallisation of the salt mixtures. The changes in σ and the limiting surface activity when various salts were added were compared with the values of the generalised moments of the ions according to the theory of Semenchenko[8,31]:

$$\mu = z/r, \qquad (1)$$

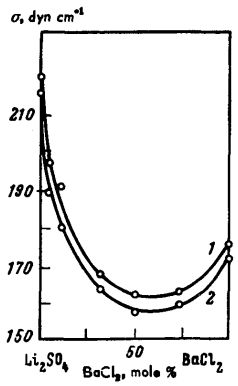

Fig. 2. Surface tension isotherms for the Li_2SO_4–$BaCl_2$ system[29,30]: 1) 1000°; 2) 1050°.

where z is the charge and r the radius of the ion. The adsorption of the surface-active components was calculated for a number of dilute mixtures.

King[32] measured σ for silicate systems up to 1600° using the hollow-cylinder detachment method which is a modification of the ring detachment method[7]. The values of σ were measured for 26 melts from the CaO–SiO_2, MgO–SiO_2, MnO–SiO_2, and FeO–SiO_2 systems, including some metasilicate compositions. Positive temperature coefficients of σ were observed for $CaSiO_3$, $MnSiO_3$, and a number of mixtures of the systems studied. This phenomenon was explained on the basis of theories regarding the breakdown of the structure of the melt. With increase in temperature the process of structure breakdown is displaced in such a way that the proportion of surface-active ions (SiO_3^{2-}) in the melt decreases; the resulting increase in σ is greater than the decrease in σ due to the decrease in the strength of the interaction between the particles with increase in temperature.

Mention may be made to the work of Shartsis and coworkers, who used the hollow-cylinder detachment method to measure σ for MO–SiO_2 (M = Li, Na, K, and Pb)[33,34] and MO–B_2O_3 (M = Li, Na, K, Ca, Sr, Ba, Zn, and Pb)[35-38] systems. The compositions of a number of systems were not brought to the metasilicate and metaborate compositions because of the limited miscibility of the components in the liquid phase.

Vajna[39] used the ring detachment method to measure σ for melts of pure cryolite and cryolite containing NaF, AlF_3, Al_2O_3, and CaF_2 additions (up to 15 wt.%).

Gromakov[40], who measured σ using Jaeger's method[15], proposed that the maximal pressures in the gas bubble be determined at two different depths of immersion of the end of the capillary in the melt, in order to eliminate the value of the density of the melt from the formula used in the calculation; this makes sense when the densities are unknown, although the error in the estimation of the density by this method is extremely large. Gromakov[41] also proposed a method for measuring the σ of small quantities of liquid by means of a capillary with thickened walls in the lower section; it was estimated that the error in the determination of σ is 10%. This method was used by Gromakov and Kostromin[42] to measure σ for a number of compositions of the $NaNO_3$–KNO_3–$RbNO_3$ ternary system.

The surface tension of systems formed by molten nitrates was also studied by Bokhovkin[43] ($AgNO_3$–KNO_3) and Manakin[44] ($NaNO_3$–KNO_3, $LiNO_3$–$NaNO_3$, and $LiNO_3$–KNO_3) by the maximum gas-bubble pressure method. In all the σ isotherms for the nitrate systems are either linear or only slightly convex towards the composition axis.

Peake and Bothwell[45] used the maximum gas-bubble pressure method to measure σ for the $BaCl_2$–KCl system, for which the 800° isotherm has a point of inflection corresponding to 35 mole % $BaCl_2$ (Fig. 3).

Peake and Neithamer[46] determined σ for the KCl–K_2SO_4 system; the isotherm is convex towards the composition axis.

Desyatnikov[47] used the maximum pressure and ring detachment methods to measure σ for NaCl, KCl, and $MgCl_2$ melts; the NaCl–KCl, NaCl–$MgCl_2$ and KCl–$MgCl_2$ binary systems; and sections of the NaCl–KCl–$MgCl_2$ ternary system at molar ratios NaCl : KCl = 1 : 3, 1 : 1, and 3 : 1. The σ isotherms for the NaCl–$MgCl_2$ and KCl–$MgCl_2$ systems show breaks (Fig. 4). The values of σ obtained for $MgCl_2$ are more reliable than those given by Zhivov[19].

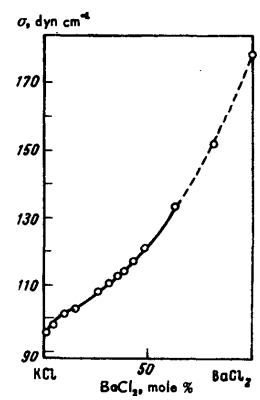

Fig. 3. 800° surface tension isotherm for the KCl–$BaCl_2$ system[45].

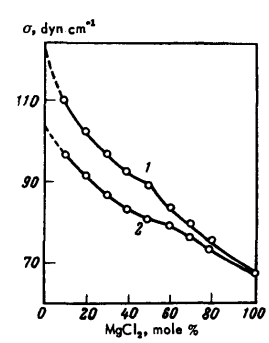

Fig. 4. 700° surface tension isotherm for the NaCl–$MgCl_2$ (1) and KCl–$MgCl_2$ (2) systems[47].

Strelets, with Desyatnikov[48,49] and Bondarenko[50,51] measured σ for the salt mixtures used in the electrolytic production of magnesium. The values of σ were measured from melts of an isoconcentrate section (10 wt.% $MgCl_2$) of the $MgCl_2$–$CaCl_2$–KCl–NaCl system at NaCl : KCl ratios of 1 : 6, 1 : 3, 1 : 1, and 6 : 1, and of isoconcentrate sections (10 wt.% and 20 wt.% $MgCl_2$) of the $MgCl_2$–$BaCl_2$–KCl–NaCl system at NaCl : KCl ratios of 2 : 1, 1 : 1, and 1 : 2, and also of the $BaCl_2$–$MgCl_2$, $BaCl_2$–NaCl, and $MgCl_2$–$BaCl_2$–NaCl (8 sections at 10 wt.% $BaCl_2$ intervals) systems. The isotherm for the $BaCl_2$–$MgCl_2$ system shows an inflection at 10–15 mole % $BaCl_2$ (Fig. 5); this is attributed to compound formation.

Bordman and coworkers[52] used the maximum gas-bubble pressure method in a glass apparatus to measure σ for 13 binary systems formed by salts with common cations or anions: AgCl–AgBr, AgBr–AgI, NaBr–KBr, KCl–KBr, $NaNO_3$–KNO_3, $CdCl_2$–$CdBr_2$, $PbCl_2$–NaCl, $PbCl_2$–$CdCl_2$, $CdCl_2$–KCl, $PbCl_2$–KCl, $PbCl_2$–AgCl, AgCl–KCl, and AgBr–KBr. The isotherms for most of the systems are linear or slightly convex towards the composition axis. The 600° isotherm for the $PbCl_2$–KCl system has a minimum at 40 mole % $PbCl_2$; this minimum is now shown by the 500° isotherm (Fig. 6). The 700° isotherm for the $CdCl_2$–KCl system passes through a maximum at 80 mole % $CdCl_2$ and through a point of inflection at the equimolar component ratio (Fig. 7). These points on the σ isotherms were attributed to the presence of ionic complexes of the type MCl_3^- in the melts. As a criterion for ideal behaviour in the binary system the authors used Zhukhovitskii's equation[53], rewritten by Guggenheim[54] for an equimolar mixture in the form

$$\sigma = {}^1/_2(\sigma_1 + \sigma_2) - (\sigma_2 - \sigma_1)^2 a/8kT, \qquad (2)$$

where σ, σ_1, and σ_2 are the surface tensions of the mixture and the pure components, k is the Boltzmann constant, and a the mean area occupied by a molecule in the surface layer, assumed to be equal to the sum

$$a = {}^1/_2\left(\frac{M_1}{d_1 N}\right)^{2/3} + {}^1/_2\left(\frac{M_2}{d_2 N}\right)^{2/3}, \qquad (3)$$

where M_1, M_2, d_1, and d_2 are the molecular weights and densities of the components, and N is Avogardro's number. For all the systems studied, with the exception of the $PbCl_2$–$CdCl_2$ system, the experimental value of σ shows a negative (up to 4%) deviation from the value calculated from Eqn. (2)†.

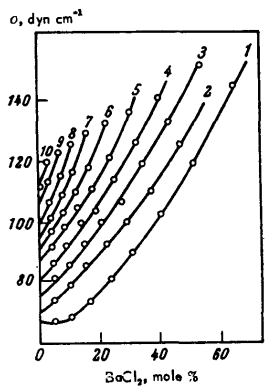

Fig. 5. 750° surface tension isotherms for $MgCl_2$–NaCl–$BaCl_2$ systems[50,51]. NaCl concentration (wt.%): 1) 0; 2) 10; 3) 20; 4) 30; 5) 40; 6) 50; 7) 60; 8) 70; 9) 80; 10) 90.

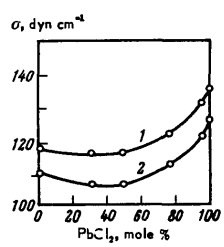

Fig. 6. Surface tension isotherms for the KCl–$PbCl_2$ system[52]: 1) 500°; 2) 600°.

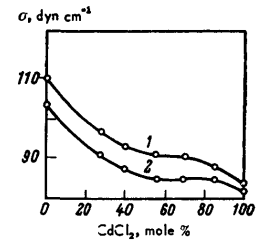

Fig. 7. Surface tension isotherms for the KCl–$CdCl_2$ system[52]: 1) 600°; 2) 700°.

Callis and coworkers[55] used the ring detachment method to determine σ up to 1000° for sodium phosphate melts at Na_2O/P_2O_5 oxide ratios from 1 to 2.2, that is, including sodium meta- and pyro-phosphates. The values of σ and $d\sigma/dt$ differ considerably from those given by Jaeger[15]. It was found that the value of σ is higher, the higher the concentration of basic oxide in the melt. The value obtained for σ and the densities of the melts were used to estimate the apparent molecular weights of the phosphates in the melt.

Dahl and Duke[56] used the maximum gas-bubble pressure method to determine σ for melts formed by $AgNO_3$–$NaNO_3$, $AgNO_3$–KNO_3, and $PbCl_2$–(LiCl, NaCl, KCl, RbCl, and CsCl) mixtures. In the $PbCl_2$–MCl systems the nature of the σ isotherms at 575° changes with increase in the dimensions of the alkali metal ion. Thus in the $PbCl_2$–LiCl system the isotherm is linear and in the $PbCl_2$–NaCl system the isotherm is convex towards the composition axis and does not show the minimum reported by Barzakovskii[25]; the σ isotherms for the $PbCl_2$–(KCl, RbCl, and CsCl) systems have minima which become deeper on going from potassium to caesium (Fig. 8). The values of σ for silver nitrate are anomalously high. The

† Conclusions regarding the extent of the deviation from ideal behaviour shown by a system on the basis of calculations from Eqn. (2) for the equimolar composition alone can of course be only approximate.

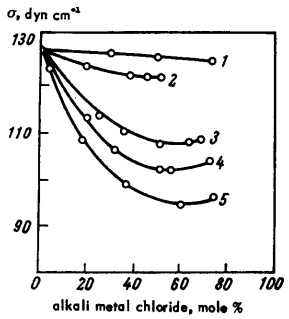

Fig. 8. 575° surface tension isotherms for the $PbCl_2$–(LiCl, NaCl, KCl, RbCl, and CsCl) systems [56]:
1) LiCl; 2) NaCl; 3) KCl; 4) RbCl; 5) CsCl.

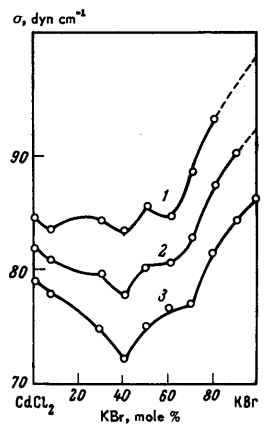

Fig. 9. Surface tension isotherms for the KBr–$CdCl_2$ system [59]:
1) 600°; 2) 700°; 3) 800°.

values of σ for $ZnCl_2$ melts are lower than those for melts formed by LiCl, NaCl, KCl, $PbCl_2$, $NaNO_3$, KNO_3, and $AgNO_3$ [57].

Ellis et al.[58] measured σ for the alkaline earth metal halides $BaBr_2$, $SrCl_2$, $SrBr_2$, $CaBr_2$, and CaI_2. For these salts, σ increases with increase in the dimensions of the cation. Ellis and coworkers[59] also studied σ for a diagonal section of the $CdCl_2$–KBr ternary reciprocal system. The σ isotherms showed a minimum at 40 mole % KBr and a point of inflection at 60 mole % KBr (Fig. 9), indicating, in the opinion of the authors, the existence of ionic complexes $CdCl_4^{2-}$ and $CdBr_4^{2-}$ in the melts; this was confirmed by the Raman spectra. The increase in the depth of the minimum on the isotherms with increase in temperature is related to the increase in the disorder and variety of the species in the melt.

Greenwood and Wade[60] determined σ for $GaCl_3$ melts and Greenwood and Worrall[61] determined σ for $GaBr_3$ and Ga_2Cl_4 melts.

Bradbury and coworkers[62,63] used the hollow-cylinder detachment method to measure σ for melts of the Na_2O–P_2O_5, K_2O–P_2O_5, and CaO–P_2O_5 binary systems from the metaphosphate composition to the pyrophosphate composition (with the exception of the CaO–P_2O_5 system) and also for $NaPO_3$ + NaF mixtures (up to 15 mole % NaF). The surface tension of the melts in all the systems increases with increase in the concentration of basic oxide or NaF in the mixture; by analogy with the silicates[32], this was attributed to breakdown of the structure of the melt‡.

Frame and coworkers[68] give values of σ for the low-melting salts KCNS, $NaNO_2$, $K_2Cr_2O_7$, and $KClO_3$, obtained by Sugden's version of the maximum gas-bubble pressure method[24]. For these salts (with the exception of $NaNO_2$) σ and σ/dt are not constant and depend on the temperature and the time for which the salt is kept above its melting point. This is related to possible decomposition of the salt or to bond redistribution. Comparison of the values of σ for alkali metal halides and nitrates shows that the influence of the dimensions of the cation is greater, the smaller the anion.

Bloom and coworkers[69] used the maximum gas-bubble pressure method to measure the surface tension of melts formed by NaCl, NaBr, NaI, KCl, KBr, KI, $NaNO_3$, $NaNO_2$, KNO_3, $AgNO_3$, $PbCl_2$, the binary $NaNO_3$–$NaNO_2$, KNO_3–KNO_2, $NaNO_3$–$AgNO_3$, KNO_3–$AgNO_3$, and $PbCl_2$–NaCl systems, and a diagonal section of the ternary reciprocal KCl–NaI system. It was suggested that the deviation of the values of σ for the salt mixtures from the values corresponding to ideal solutions be explained on the basis of theories of the surface enthalpy of mixing H^S:

$$H^s/a = \sigma - Td\sigma/dT, \qquad (4)$$

where a is the surface area and $d\sigma/cT = -\Delta S^S/a$. The formation of an ionic complex in the melt leads to a decrease in enthalpy in the bulk phase and also to a decrease in the surface enthalpy of mixing:

$$\Delta\sigma = \Delta H^s/a - T\Delta S^s/a, \qquad (5)$$

that is, when an ionic complex is formed $\Delta\sigma < 0$, if $\Delta H^S/a < 0$ and $\Delta S^S/a > 0$. For the $NaNO_3$–$AgNO_3$ and $PbCl_2$–NaCl systems, small negative deviations from the values for ideal mixtures (~ 7%) were observed. For the KCl–NaI, $PbCl_2$–RbCl[56], and $CdCl_2$–KCl[52] systems, the curves obtained by plotting $\Delta H^S/a$ against the mole fraction of the second component show maxima corresponding to 50 mole % NaI and RbCl and 75 mole % KCl. Generally speaking, the method for estimating $\Delta H^S/a$ assumed that $d\sigma/dT$ is constant over a wide temperature range, and the use of the values of $d\sigma/dT$ to calculate $\Delta H^S/a$ requires that σ be measured with a fairly high accuracy, and this is not always true.

Popel' and Esin[70] measured σ for the CaO–SiO_2–Al_2O_3 and CaO–SiO_2–MgO ternary oxide systems by stationary-drop and maximum gas-bubble pressure methods; values of σ were obtained for calcium metasilicate in the range 1460–1520°. The same methods were used by Manakov and coworkers[71] to determine σ for potassium metaniobate at 1400°.

Lantratov[72] used the gas-bubble pressure method to measure σ for melts formed by the salt systems used as electrolytes in the preparation of metallic sodium. The

‡ In systems of the type MPO_3–MX (where X = halide, SO_4^{2-}, etc.), chemical reaction takes place, accompanied by the separation of reaction products[64–67]. Bradbury and coworkers[62,63] apparently made no allowance for this feature and measured σ for non-equilibrium mixtures of indefinite composition.

$CaCl_2$–NaCl binary system and sections of the $BaCl_2$–$CaCl_2$–NaCl ternary system at $CaCl_2$: $BaCl_2$ ratios of 3 : 1 and 3 : 2 were studied. NaF and CaF_2 additives (up to 10 wt. %) were found to be surface-inactive with respect to these systems.

Janz and Lorenz[73,74] measured σ for aggressive carbonate melts up to 1000° in an atmosphere of CO_2 by the solid detachment method[7]. The solid detached from the surface consisted of the elongated tip of a gold–palladium sphere, which was also used to determine the density. Values of σ were obtained for melts formed by Li_2CO_3, Na_2CO_3, K_2CO_3, and the Na_2CO_3–K_2CO_3 binary system.

Addison and Coldrey[75] used the gas-bubble pressure method to measure σ for molten $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$, $TlNO_3$, NH_4NO_3, $AgNO_3$, $NaNO_2$, and KNO_3. The values of σ found for $TlNO_3$ were 25% lower than those given by Jaeger[15]. The values of σ for the molten nitrates and chlorides of the alkali and alkaline earth metals and magnesium close to the melting points were compared with the radii of the cations: the values of σ for the alkali metal salts decrease from Li to Cs; the values of σ for the alkaline earth metal salts increase from Mg to Ba (Fig. 10). This nature of the change in σ was attributed to the increase in the covalent forces in the subgroup formed by the alkaline earth metals and magnesium.

Morris and coworkers[76] used an assembly similar to that described by Janz and Lorenz[73] to measure σ for the $PbMoO_4$–$Bi_2(MoO_4)_3$ system. The temperature coefficients $d\sigma/dt$ for all compositions change with change in temperature.

Lehman[77] measured σ for melts of the KCl–$CaCl_2$ and CsCl–$CaCl_2$ systems§.

Sokolova and Voskresenskaya[78–80] used the maximum gas-bubble pressure method to study σ for the NaCl–$BaCl_2$ system and for the NaBr–K_2SO_4 diagonal section of the Na, K ‖ Br, SO_4 ternary reciprocal system. Reshetnikov's equation[81] in the form

$$\sigma = \sigma_1 + \frac{(\sigma_2 - \sigma_1)x}{x + k(1-x)}, \qquad (6)$$

where σ, σ_1, and σ_2 are the surface tensions of the mixture and the pure components, x the mole fraction of the second component, and k a constant, is applicable to the isotherms.

Sokolova and coworkers obtained values of σ for the metaphosphates of lithium, sodium, potassium, caesium, calcium, strontium, and barium[82] and the $LiPO_3$–$NaPO_3$, $NaPO_3$–$Ca(PO_3)_2$, and KPO_3–$Ba(PO_3)_2$ binary systems[83]. These and published data were used to construct curves giving the dependence of σ on the generalised moments μ — see Eqn. (1) — of the cations and anions forming the salt[82,84] (Figs. 11 and 12). The nature of the change in the dependence of σ on μ for the cation of the alkaline earth metal salts was compared[82] with the possible difference in the degree of dissociation of these salts[85] and the existence of MX^- ions in the melts. The values for some radium salts were estimated by interpolation from the plots of σ against μ. On the basis of the experimental facts it was suggested[84] that the values of σ for the alkali metal metaphosphates are independent of the length of the $(PO_3^-)_n$ polyanion chain and that a decisive part is played by the terminal PO_4^{2-} groups. Values of σ were determined for zinc metaphosphate and the binary $NaPO_3$–$Zn(PO_3)_2$ and KPO_3–$Zn(PO_3)_2$ systems (Figs. 13 and 14), for which the equilibrium diagrams were also studied[86]. The same authors[87] also studied σ for a number of nitrate and nitrite–nitrate salt mixtures.

Wu and coworkers[88] used the maximum gas-bubble pressure method to study σ for the FeO–Fe_2O_3–P_2O_5 system (up to 20 mole % P_2O_5), a number of (FeO–Fe_2O_3)–CaO–P_2O_5 mixtures, and the CaO–P_2O_5 system up to the metaphosphate composition.

Yakobashvili and Frumin[89,90] used the drop-weight method to obtain the values of σ for pure CaF_2 and for CaF_2 containing added CaO, MgO, SiO_2, ZrO_2, TiO_2, and Al_2O_3.

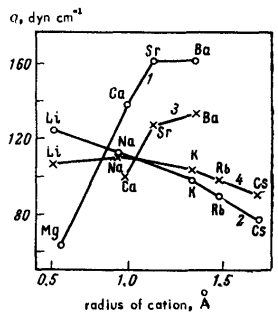

Fig. 10. Dependence of the surface tension of the chlorides and nitrates of the alkali and alkaline earth metals and magnesium on the radius of the cation[75]:
1) Group II chlorides at 1000°; 2) Group I chlorides at 800°; 3) Group II nitrates close to the melting point; 4) Group I nitrates at 425°.

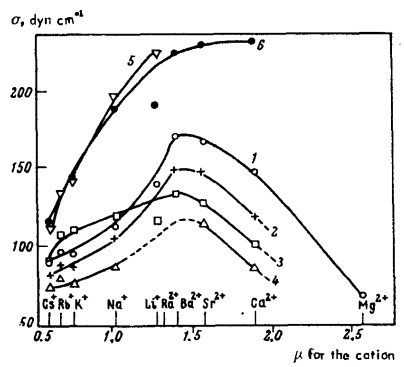

Fig. 11. Dependence of the surface tension of salts of the alkali and alkaline earth metals and magnesium at the melting points on the generalised moments of the cations[82]:
1) chlorides; 2) bromides; 3) iodides; 4) nitrates; 5) sulphates; 6) metaphosphates.

§ We have no information on the method of measurement or the shape of the σ isotherms, since only an abstract was available.

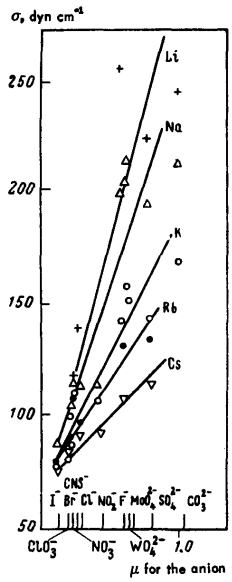

Fig. 12. Dependence of the surface tension of alkali metal salts at the melting point on the generalised moments of the anions [84].

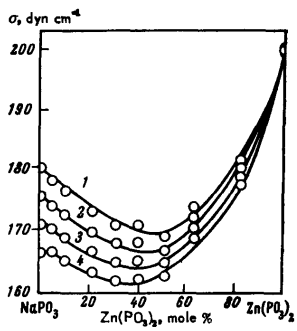

Fig. 13. Surface tension isotherms for the $NaPO_3$–$Zn(PO_3)_2$ system [86]:
1) 800°; 2) 900°; 3) 1000°: 4) 1100°.

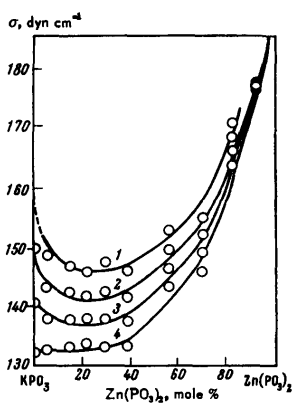

Fig. 14. Surface tension isotherms for the KPO_3–$Zn(PO_3)_2$ system [86]:
1) 800°; 2) 900°; 3) 1000°; 4) 1100°.

Nikitin and coworkers [91] used the stationary-drop method to determine the values of σ for pure CaF_2 and for CaF_2 containing added CaO, SiO_2, Al_2O_3, and MgO in the range 1470–1550°.

Moiseev and Stepanov [92] used the maximum gas-bubble pressure method in an atmosphere of CO_2 to measure σ for melts formed by Li_2CO_3, Na_2CO_3, K_2CO_3, and the binary systems and the ternary system based on these carbonates.

Owens and Mayer [93] determined the values of σ for $NaPO_3$–Li_2SO_4, $NaPO_3$–Na_2SO_4, $NaPO_3$–Rb_2SO_4, and $NaPO_3$–UO_2SO_4 mixtures; as in the work of Bradbury and coworkers [62,63], no allowance was made for possible chemical interaction between the components [65], leading to the liberation of SO_3.

Campbell and Williams [94] used the maximum gas-bubble pressure method in the range 130–170° to determine σ for $LiClO_3$ and its mixtures with H_2O (up to a mole fraction of 0.236) and with $LiNO_3$ (up to a mole fraction of 0.213).

Bertozzi and Sternheim [95] used the solid detachment method [7] to determine σ for 13 binary systems formed by the nitrates of the alkali metals and silver.

Mellors and Senderoff [96] studied σ for melts formed by the NaF–LiF–ZrF_4 ternary system (from 2.9 mole % to 60 mole % ZrF_4 in mixtures with the eutectic NaF : LiF = = 2 : 3) in the range 750–850°. On the basis of a comparison of σ and the surface enthalpy H^s/a (4) with the logarithm of the ZrF_4 concentration, it was concluded that the melts contain the $[ZrF_7]^{3-}$ ion. The $[ZrF_6]^{2-}$ ion, which is stable in the solid state, was not detected in the melts.

III. SURFACE TENSION OF ONE-COMPONENT SALT SYSTEMS

1. Surface Tension of Molten Salts at the Melting Point

Examination of the literature on the surface tension of molten salts shows that up to the present, values of σ have been determined more or less reliably for almost a hundred individual salts.

In Table 1 we have collected the published values of σ for pure salts at the melting point or at temperatures close to the melting point. The melting points were taken from various sources [15,68,97] and the surface tension values are those of Jaeger [15] and later workers, since the reliability of the results of earlier studies [5,6,9–14] is doubtful. Some of the values of σ given in Table 1 were obtained by analytical or graphical extrapolation from published data. The values of σ given in Table 1 were obtained with different degrees of experimental accuracy, which in a number of specific instances could not be estimated. In most instances the error in the determination of σ apparently amounts to not less than ±1% of the measured quantity, particularly in the high-temperature range.

2. Temperature Dependence of the Surface Tension of Molten Salts

The investigation of the temperature dependence of the surface tension of molten salts is one of the important problems associated with the surface properties of melts.

TABLE 1. Surface tension of molten salts at the melting point.

Salt	M.p., °C	σ, dyn cm⁻¹	Refs.
Lithium salts			
LiF	840	255.2	15
LiCl	680	140.2	15
$LiNO_3$	254	118.4	15
		115.4	75
Li_2CO_3	726	244.1	74,92
Li_2SO_4	852	224.4	15
		226	29,30
$LiBO_2$	845	264.8	15
$LiSiO_3$	1201	381	15
	at 1200	~355	34
$LiPO_3$	675	191.1	82
$LiClO_3$	128	88.6	94
Sodium salts			
NaF	990	201.6	15
NaCl	801	114.1	15,19,26, 28,76
		116.4	69,2,3
NaBr	768	106.5	15
		98	69
	at 755	102.8	79
NaI	660	88.2	15,69
$NaNO_2$	281	124.5	68
		119.4	69
	277	121.2	75
$NaNO_3$	312	120.7	15
		119.0	27
		116.9	52
		116.6	75
		113	2,3
			см.[42–44]
Na_2CO_3	858	211.7	74,92
Na_2SO_4	884	196.3	15
	at 900	192.6	29,30
Na_2MoO_4	687	215.1	15
Na_2WO_4	694	204.4	15
$NaPO_3$	620	209.5	15
		194	55
		192.5	62,63
	623,5	189.5	82
$Na_4P_2O_7$	994	248	55
		~243	63
$NaBO_2$	965	201.6	15
Na_2SiO_3	at 1570	307	32
	at 1100	300	34
Na_3AlF_6	1000	145.5	21
Potassium salts		148.3	39
KF	858	143.2	15
KCl	at 800	96.1	25
	780	97.4	15,19,29,45
		98.3	69
KBr	734	88.8	15,29
		90.6	59
		89.5	69
KI	681	78.3	15,29
		79.5	69
KNO_2	435	107.6	75
KNO_3	339	112.9	15
		109.3	69,2,3
		113.5	56
	334	110.8	75
$CaSiO_3$	at 1570 in the range 1460–1520	400 465	32 70
Strontium salts			
$SrCl_2$	873	169.0	58
$SrBr_2$	643	149.5	58
SrI_2	507	115.0	75
$Sr(NO_3)_2$	at 615	128.4	82
$Sr(PO_3)_2$	1010	228.3	
Barium salts			25
$BaCl_2$	at 1000	171.0	29
	962	177	45
		165	79
	960	170	58
$BaBr_2$	847	153	75
$Ba(NO_3)_2$	595	134.8	82
$Ba(PO_3)_2$	868	224.5	
Copper salts			99
CuCl	at 450	95	
Silver salts			52,3
AgCl	455	179	52,3
AgBr	434	154	52
AgI	552	116	15
$AgNO_3$	212	170.2	43
		171	56
		150	69
		148	75
		152.1	
Zinc salts			
$Zn(BO_2)_2$	at 900	130	36
$Zn(PO_3)_2$	862	199.2	86
Cadmium salts			
$CdCl_2$	568	90	52,3
K_2CO_3	899	168.2	74,92
K_2SO_4	1069	144.5	15
		144	30
		142.3	46
		137	79
K_2MoO_4	919	152.5	15
K_2WO_4	921	158.2	15
$K_2Cr_2O_7$	396	140	15
		129	68
$KClO_3$	368	84	15
		81	68
KCNS	173	101.5	68
KPO_3	820	161.2	15
	810	140.0	63
		148.2	82
$K_4P_2O_7$	1090	~185	63
KBO_2	946	136.6	15
$K_3Nb_2O_6$	1400	150	71
Rubidium salts			
RbF	765	132.0	15
RbCl	720	98.3	15,29
RbBr	685	90.7	15
RbI	642	80.3	15
$RbNO_3$	304	109	15,43,75
Rb_2SO_4	1055	135	15
Caesium salts			
CsF	692	107.1	15
CsCl	646	91.3	15
		93	29
CsBr	631	83.6	15
CsI	620	75.4	15
$CsNO_3$	414	92.0	15
		92.5	75
Cs_2SO_4	1015	113.1	15
$CsPO_3$	724	118.0	82
Ammonium salts			
NH_4NO_3	170	101.9	75
		99.7	98
Magnesium salts			
$MgCl_2$	at 733	135.8	19
	at 750	~68	47,48
$MgSiO_3$	at 1570	378	32
Calcium salts			
CaF_2	in the range 1470–1550	280	91
	at 1400	400	90
$CaCl_2$	772	148.6	25,26,48–51,72
$CaBr_2$	730	119.6	58
CaI_2	740	85.8	58
$Ca(NO_3)_2$	at 560	101.6	75
$Ca(PO_3)_2$	969	229.6	63
		230.2	82
	at 1025	~235	88
$CdBr_2$	567	~70	52
		86	58
Mercury salts			
$HgCl_2$	at 293	56.1	23
$HgBr_2$	at 241	64.5	23
Gallium salts			
$GaCl_3$	77.7	27.3	60
Ga_2Cl_4	172.4	56.2	61
$GaBr_3$	122.5	35.2	61
Thallium salts			
$TlNO_3$	206	117.5	15
		94.8	75
Tin salts			
$SnCl_2$	250	100	15
Lead salts			
$PbCl_2$	501	142.8	25
		136	52,56,3
		137	69
$PbMoO_4$	1090	166.0	76
$Pb(BO_2)_2$	at 900	100	36
$PbSiO_3$	at 1000	~240	33
Antimony salts			
$SbCl_3$	73.2	50	15
Bismuth salts			
$BiCl_3$	233	71.2	15
$Bi_2(MoO_4)_3$	630	165	76
Manganese salts			
$MnSiO_3$	at 1570	415	32
Iron salts			
$FeSiO_3$	at 1570	363	32

The values of the temperature coefficients for molten salts are often not indicated at all, or are given with no estimate of the accuracy of the determination; this applies to an even greater extent to the temperature coefficients for salt mixtures. In the present review, therefore, we shall restrict ourselves to general points. The surface tension of most of the salts studied decreases with increase in temperature; the course of the σ polytherms is given by the equation $\sigma = a - bt$, where a and b are empirical constants. Almost invariably the absolute value of $b = -d\sigma/dt$ does not exceed 0.1 dyn cm^{-1} deg^{-1}. For some salts, however, the values of $d\sigma/dt$ are close to zero (for example, $MgCl_2$ [20,47] and metaphosphates [82]) or even positive (silicates [32]). This phenomenon is apparently due to a change in the structure of the melts with increase in temperature (decrease in the size of the particles, dissociation), leading to the accumulation of surface-inactive particles in the melt [32,82]. The values of $d\sigma/dt$ are generally constant within the temperature ranges studied, but in a number of instances it has been found that the values of $d\sigma/dt$ are not constant, for example, for certain fluorides, nitrates, sulphates [15], molybdates [73], the low-melting $KClO_3$, KCNS, and $K_2Cr_2O_7$ [68], and Na_3AlF_6 [22]. It is possible that in some instances this is due to decomposition of the salts, leading to a change in composition.

IV. SURFACE TENSION OF BINARY SALT SYSTEMS

In the study of the surface tension of binary system, the problems of the nature of the shapes of the σ isotherms and their classification, interpretation, and analytical expression are of greatest interest. Despite the general character of these problems for binary systems of different type (organic, metallic, oxide, salt, etc.), they cannot yet be regarded as completely solved. In particular, the extent to which the value of σ for binary systems is sensitive to change in the structure of the bulk phase and the correspondence between the shape of the σ isotherms and the interaction between the components of the melt, reflected by the equilibrium diagram, are not yet clear. It is not possible in the present paper to examine in detail the literature dealing with all these problems. Of the most interesting topics we may mention the studies of Trifonov [100] (the general classification of σ isotherms for binary organic systems) and Teitel'baum [101] (factors influencing the shape of σ isotherms), the Zhukhovitskii [53]–Guggenheim [54] equation mentioned above, and the work of Esin [102] (oxide systems) and Eremenko and coworkers [103] (metallic systems).

Since information on σ isotherms has been published for more than 50 binary salt systems, it was of interest to use this material to investigate the correspondence between the shape of the σ isotherms and the equilibrium diagrams. For this purpose we compared the σ isotherms and equilibrium diagrams for three groups of binary salt systems (Tables 2–4); the fusibility data were taken from a handbook [104] and the concentrations of the components are given in mole fractions or mole %.

1. Binary Salt Systems with the Formation of Solid Solutions or Eutectics

Of the 26 binary salt systems in the first group, 25 of the systems give isotherms which are linear or convex towards the composition axis (Table 2). In accordance

TABLE 2. Binary salt systems with formation of solid solutions or eutectics

System	Type of equilibrium diagram (Ref. 104)	Shape of σ isotherm	Refs.
LiCl—RbCl	eutectic	convex towards composition axis	30
LiCl—$PbCl_2$	»	linear	56
$LiNO_3$—$NaNO_3$	»	ditto	44
$LiNO_3$—KNO_3	solid solutions with minimum	convex towards composition axis	44,52
$LiPO_3$—$NaPO_3$*	?	ditto	83
NaCl—KCl	solid solutions	linear, convex towards the K composition axis	19,25,47
NaCl—$CaCl_2$	eutectic	convex towards composition axis	25,26,72
NaCl—$BaCl_2$	»	ditto	25,79
NaCl—$PbCl_2$	»	» with a minimum	25,26,56,69
NaBr—KBr	solid solutions with a minimum	convex towards composition axis	52
$NaNO_2$—$NaNO_3$	ditto	ditto	69
$NaNO_2$—KNO_3	»	linear	44,52
$NaNO_3$—$RbNO_3$	solid solutions	convex towards composition axis	42
$NaNO_3$—$AgNO_3$	solid solutions with a peritectic	ditto	56,69
Na_2CO_3—K_2CO_3	solid solutions with a minimum	»	74,92
KCl—KBr	ditto	»	52
KCl—AgCl	eutectic		52
KCl—K_2SO_4	solid solutions with a minimum	»	46
KBr—AgBr	ditto	»	52
KNO_3—KNO_2	»	»	69
KNO_3—$RbNO_3$	solid solutions with a minimum	convex towards composition axis	42
AgCl—AgBr	ditto	ditto	52
AgCl—$PbCl_2$	eutectic		52
AgBr—AgI	solid solutions with a minimum	convex towards composition axis	52
$CdCl_2$—$CdBr_2$	ditto	ditto	52
$CdCl_2$—$PbCl_2$	eutectic	»	52

* System assigned conditionally to Group I.

TABLE 3. Binary salt systems with compound formation.

System	Compound (Ref. 104)	Shape of σ isotherm	Refs.
Li_2CO_3—Na_2CO_3	$Li_2CO_3 \cdot Na_2CO_3$	convex towards composition axis	92
Li_2CO_3—K_2CO_3	$Li_2CO_3 \cdot K_2CO_3$	ditto	92
NaCl—$MgCl_2$	$NaCl \cdot MgCl_2$;	inflection at 50 mole % $MgCl_2$, maximum at 86 mole % $MgCl_2$	20,47
	$2NaCl \cdot MgCl_2$	inflection at 50 mole %	
NaCl—$CdCl_2$	$2NaCl \cdot CdCl_2$	convex towards composition axis	52
$NaPO_3$—$Ca(PO_3)_2$	$4NaPO_3 \cdot Ca(PO_3)_2$	ditto	83
$NaPO_3$—$Zn(PO_3)_2$	$NaPO_3 \cdot Zn(PO_3)_2$	minimum at 50 mole %	86
KCl—$MgCl_2$	$KCl \cdot MgCl_2$; $2KCl \cdot MgCl_2$	inflection at 50 mole %	20,47
KCl—$CaCl_2$*	$KCl \cdot CaCl_2$	?	77
KCl—$BaCl_2$	$KCl \cdot BaCl_2$ or $2KCl \cdot BaCl_2$	inflection at 35 mole % $BaCl_2$	45
KCl—$CdCl_2$	$KCl \cdot CdCl_2$; $4KCl \cdot CdCl_2$	inflection at 50 mole % KCl, maximum at 20 mole % KCl	52
KCl—$PbCl_2$	$KCl \cdot PbCl_2$; $2KCl \cdot PbCl_2$	minimum at 55 mole % KCl	52,56
KNO_3—$AgNO_3$	$KNO_3 \cdot AgNO_3$	convex towards composition axis	43,56,69
KPO_3—$Ba(PO_3)_2$**	?	inflection at 70–80 mole % KPO_3	83
KPO_3—$Zn(PO_3)_2$	$KPO_3 \cdot Zn(PO_3)_2$	minimum at 70 mole % KPO_3	86
RbCl—$PbCl_2$	$RbCl \cdot 2PbCl_2$; $RbCl \cdot PbCl_2$; $2RbCl \cdot PbCl_2$	minimum at 55 mole % RbCl	56
CsCl—$CaCl_2$*	$CsCl \cdot CaCl_2$	?	77
CsCl—$PbCl_2$	$xCsCl \cdot yPbCl_2$; $CsCl \cdot PbCl_2$	minimum at 55 mole % CsCl	56
$MgCl_2$—$BaCl_2$	compound of unknown composition	inflection at 15 mole % $BaCl_2$	50,51

* Shape of σ-isotherm for the system not known to us (see footnote on p. 505).

** System assigned conditionally to Group II.

TABLE 4. Diagonal sections of ternary reciprocal systems.

System	Type of diagonal	Shape of σ isotherm	Refs.
Li_2SO_4—NaCl	stable diagonal	convex towards composition axis	29
Li_2SO_4—KCl	ditto	ditto	29
Li_2SO_4—RbCl	from ΔH – stable diagonal of singular system	»	29
Li_2SO_4—CsCl	reversibly-reciprocal system	»	29
Li_2SO_4—$BaCl_2$	from ΔH – stable diagonal	minimum at 30 mole % $BaCl_2$	29
		minimum at 15 mole % KCl	69
NaI—KCl	unstable diagonal		
NaBr—K_2SO_4	from ΔH – unstable diagonal	convex towards composition axis	79
KBr—$CdCl_2$	from ΔH – unstable diagonal	inflection at 60 mole % KBr, minimum at 40 mole % KBr	59

with conclusions from the Zhukhovitskii equation[53], linear isotherms are observed when the values of σ for the pure components are close to one another. In this group a minimum is observed only on the σ isotherms for the NaCl–$PbCl_2$ system. Electrical conductivity and e.m.f. data for this system[105] suggest that the melts contain unstable ionic complexes.

2. Binary Salt Systems with Compound Formation

The second group consists of binary systems for which the equilibrium diagrams indicate the formation of compounds (Table 3). This group also contains the KCl–$CaCl_2$ and CsCl–$CaCl_2$ systems, for which the nature of the isotherms is unknown[77]. This group also contains the KPO_3–$Ba(PO_3)_2$ system, for which the equilibrium diagram has not been studied but in which the possibility of compound formation is confirmed by the tendency of potassium salts to form ionic complexes with the salts of bivalent cations[2]. A characteristic feature is that the σ isotherms for 11 systems of this group show singular points (extremal points, points of inflection, and breaks), the isotherms being linear or convex towards the composition axis in only five instances. It is possible that in these last systems the compounds which crystallise from the liquid phase dissociate. The absence of interaction between the components in the liquid phases of the KNO_3–$AgNO_3$ and NaCl–$CdCl_2$ systems, whose isotherms show no singular points, is confirmed by data on a large number of their properties[2].

Thus the interaction between the components of binary salt systems, reflected by the equilibrium diagram, is in a number of instances also revealed on the σ isotherms; here the composition corresponding to a singular point on the σ isotherms does not always correspond to the composition of the compound crystallising, as is in general possible[3].

3. Diagonal Sections of Ternary Reciprocal Systems

The experimental material on σ for ternary reciprocal systems is insufficient to enable any conclusion to be reached regarding the relationships between the equilibrium diagrams and the shapes of the σ isotherms for the diagonal sections. In the third group, 8 such sections have been studied, and the diagrams are known for only 4 of these (Table 4). The classification of the remaining pairs of salts in a given system type and the form of the diagonals[106] was estimated approximately on the basis of Kablukov's rule[107] from the magnitude and sign of the heats of the exchange reactions ΔH_{298}, calculated from the heats of formation of the reacting compounds[108].

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Thus the surface tension isotherms for binary salt systems with solid solution or eutectic formation generally show no singular points; the surface tension isotherms for binary systems with interaction between the components usually show singular points — extrema, points of inflection or breaks. The surface tension of salt melts is a property which to a certain extent is sensitive to change in the structure of the melts.

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THE CYCLISATION OF ALKYNES AND THEIR DERIVATIVES

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I. INTRODUCTION

In recent years the polymerisation of alkynes has been attracting increasing attention with the discovery of new aspects of this diverse process. Up to recently, the polymerisation of acetylene yielded only oligomers of linear structure (vinylacetylene, divinylacetylene, etc.), or high-molecular products of the cuprene type. Instances of the cyclisation of acetylene with the formation of aromatic compounds, particularly benzene, were known, but the methods of synthesis were imperfect and the mechanism of synthesis was not clear. A review of the state of the problem may be found in the monograph of Newland and Vogt[1].

The cyclisation of acetylene and its derivatives was presented in a new light after Reppe's discovery of active catalysts that permit the selective preparation of the corresponding cyclic oligomers under mild conditions[2]. Later, numerous papers appeared in which catalysts suitable for the most diverse examples were recommended. Control of the course of the reactions and high yields made cyclisation a process of practical interest. It was

shown that a virtually unlimited variety of benzene derivatives could be synthesised, the preparation of which was extremely complicated by other methods. This applies, for example, to trivinylbenzene, substituted styrene, substituted divinylbenzene and similar products.

The theoretical significance of these reactions should also be considered; this is important because it makes possible the investigation of fine details of the mechanism of action of the complex catalysts that are used for the cyclisation of alkynes. It is well known that similar catalysts are widely used for the polymerisation of alkenes and alkadienes (ethylene, propene, buta-1,3-diene, isoprene) in the preparation of synthetic rubbers and plastics. However, a study of the mechanism of action of catalysts is difficult because of the complexity of the processes of formation of macromolecules of enormous molecular weight and with a fairly wide molecular-weight distribution. This complication is completely eliminated in the cyclisation of alkynes, in which individual low-molecular products are formed.

The monograph and review literature contains very little information on the cyclisation of alkynes, notwithstanding the obvious interest in the subject. In fact, that is only one review on the subject, that of Nagihara in the Japanese language, which is not accessible to a wide circle of chemists[3]. The present review is intended to fill this gap.

Berthelot was the first to describe the cyclisation of acetylene; he obtained benzene, naphthalene and other aromatic compounds by heating acetylene above 600°[4]. Later, Mayer and coworkers[5] obtained 60% conversion by passing acetylene with hydrogen through an electric furnace at 800°; benzene, naphthalene, anthracene, biphenyl, pyrene, and a number of other compounds were separated from the resinous product obtained. Zelinskii[6] obtained aromatic hydrocarbons in high yield by passing acetylene over activated carbon at 600–650°.

Newland and Vogt give a review of papers on the high-temperature cyclisation of acetylene[1]. In recent years, interest in this process has decreased, because of the discovery of catalytic methods of cyclisation at moderate temperatures. However, occasionally papers appear on the non-catalytic cyclisation of acetylene itself and its derivatives. Thus, Rupprecht[7] reports the preparation of hexadeuteriobenzene in 20% yield from deuterioacetylene at 700°. Harris and coworkers[8] obtained hexakistrifluoromethylbenzene from perfluorobut-2-yne at 260° and 1000 atm. Shantorovich and coworkers studied the thermal polymerisation of phenyl- and cyclohexyl-acetylenes and obtained the corresponding benzene derivatives[9].

Recently, a report appeared on the spontaneous cyclic oligomerisation of t-butylfluoroacetylene, which proceeds even at low temperatures[10]; the main product of this reaction is 1,2,3-tri-t-butyltrifluorobenzene.

As a rule, the high-temperature cyclisation of acetylene and its derivatives cannot be used for the purposeful synthesis of definite compounds; many different products, including high-molecular products, are obtained at the same time. These disadvantages are largely avoided when the reaction is carried out in the presence of catalysts. Cyclisation may lead to cyclic trimers, which are derivatives of benzene, or to non-benzenoid cyclic polymers (cyclobutadiene, cyclo-octatetraene, etc.). These two synthetic routes will be considered separately.

II. CATALYTIC CYCLOTRIMERISATION OF ALKYNES

1. Cyclotrimerisation in the Presence of Catalysts Based on Nickel Carbonyls

$[Ni(CO)_2[PPh_3)_2]$, formed by the reaction of $Ni(CO)_4$ with an alcoholic solution of $P(C_6H_5)_3$, which was proposed by Reppe, was one of the first catalysts for the preparation of benzene derivatives from acetylene[11]; when suspended in benzene, acetonitrile, or tetrahydrofuran, it cyclises acetylene to benzene (88%) and styrene (12%). The trimers of prop-2-yn-1-ol, 1,3,5- and 1,2,4-tri(hydroxymethyl)benzene, were obtained in quantitative yield with the same catalyst in boiling benzene. It is interesting that the ratio of the isomers in the reaction products was 1 : 1 instead of 3 : 1, as would be expected with mutual orientation of the alcohol molecules according to the laws of statistics.

Reppe did not succeed in preparing the cyclic trimer of butynediol, which he explained by the absence of unsubstituted acetylene hydrogen from this compound. However, somewhat later Kleinschmidt obtained hexa(hydroxymethyl)benzene on the same catalyst[12].

It was shown in subsequent papers that other alkynes and their derivatives can be cyclotrimerised in the presence of nickel-carbonylphosphine catalyst. Thus, Rose and Statham[13] carried out the cyclic trimerisation of phenylacetylene and phenylethynylmethanol to give 1,2,4-triphenylbenzene and 1,3,5-tri-(α-hydroxybenzyl)benzene respectively. They also attempted to obtain benzene derivatives from 3-methylbuty-1-yn-3-ol, *NN*-diethyl-1--methylprop-2-ynylamine, benzoylacetylene and phenylpropiolic acid, but they did not succeed in obtaining trimers.

The preparation of tri-(1-hydroxyethyl-1-methyl)benzene, triisopropylbenzene[15], and 1,2,4-trivinylbenzene on the same catalyst is described in a number of patents (cited by Meriwether and coworkers[14]). Simultaneous cyclotrimerisation of acetylene and divinylacetylene gave *o*-divinylbenzene[16], and *o*-xylene was obtained in the same way from acetylene and but-2-yne[17]. It is interesting that in a number of instances the use of the catalyst $[Ni(CO)_2.$ $.(PPh_3)_2]$ may lead to the formation of linear polymers.

Using 35 different mono- and di-substituted acetylenes, Meriwether and coworkers[14] studied reactions in the presence of $[Ni(CO)_2(PPh_3)_2]$. The catalyst (0.4 mole % of the monomer) and the alkyne compound were dissolved in a suitable solvent (benzene, cyclohexane, ethanol) and boiled under reflux for 24 hours. As a rule, the reaction yielded a mixture of isomers of benzene derivatives, and linear polymers of the general formulae

$$R{-}C{\equiv}C{-}[CR{=}CH]_n{-}CH{=}CHR,$$

and

$$R{-}C{\equiv}C{-}[CR{=}CH]_n{-}CR{=}CH_2,$$

where $n = 0$–10. The preferential formation of cyclic or linear products is mainly determined by the nature of the substituent at the triple bond. Thus, for monosubstituted alkynes, the yield of aromatic products fell from 65% for propyne to 5% and lower for hept-1-yne, although the total conversion remained almost unchanged. The ratio of 1,2,4-isomers to 1,3,5-isomers varied in the homologous series without showing definite tendencies. It was found that steric factors have a great effect on the reactions. Cyclohexylacetylene formed only a linear dimer, and t-butylacetylene did not react at all.

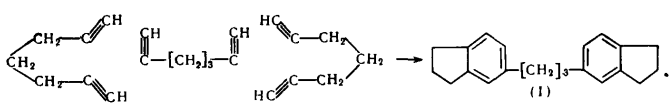
Meriwether did not succeed in polymerising more disubstituted acetylenes, conjugated diacetylenes, and also

monosubstituted acetylenes, containing t-butyl, carboxyl, amide, or nitrile groups, or halogen.

When the structures of two alkynes did not differ greatly, it was found possible to carry out simultaneous cyclotrimerisation, in particular with a mixture of hept-1-yne and pent-1-yne, or with pent-1-yne and phenylacetylene. A mixture of benzene (43%), *o*-xylene (50%), styrene, and 1,2,3,4-tetramethylbenzene was obtained by the simultaneous cyclopolymerisation of acetylene and but-2-yne.

The following qualitative order of reactivity was established for the cyclotrimerisation on $[Ni(CO)_2(PPh_3)_2]$ of alkyne ethers, esters and ketones: vinylacetylenes > > arylacetylenes > acetylene alcohols > higher alkynes > > lower alkynes, acetylene ≫ acetylenic acids.

More active monomers generally form aromatic products, and the less active more linear polymers. The cyclotrimerisation of unconjugated diacetylenes on the same catalyst is very interesting, mixed aliphatic-aromatic structures being formed[18]. Thus hepta-1,6-diyne forms, in addition to a highly unsubstituted linear polymer, an aromatic trimer, 1,3-di-(5-indanyl)-propane (I):



(I)

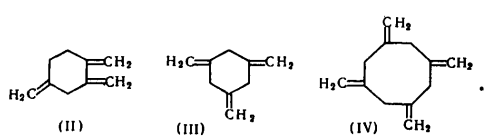
In the polymerisation of alkynes with modified catalysts, it was shown that monocarbonyltriphosphine and tetraphosphine complexes of nickel do not catalyse the cyclic polymerisation of alkynes[19]. When the phenyl group linked to phosphorus is replaced by other groups, the catalyst activity is significantly changed in the following order:

$$C_2H_4CN > C_6H_5 > H > OC_2H_5 > \text{n-alkyl} \gg OC_6H_5 \text{ and Cl.}$$

Experiments in which $Ni(CO)_4$ was used did not lead to the formation of trimers. All these results indicate the important part played by the phosphine ligands in the catalyst complex. Replacement of groups linked with phosphorus affects not only the catalyst activity but also the direction of the reaction. Thus, $[Ni(CO)_2\{P(OC_6H_5)_3\}_2]$ favours aromatisation of phenylacetylene, but $[Ni(CO)_2 \cdot \{P(C_2H_4CN)_3\}_2]$ favours linear polymerisation.

Attempts made by Meriwether and coworkers to obtain kinetic information on the cyclotrimerisation of alkynes on carbonylphosphinenickel catalysts were not successful[19]. This reaction is very rapid and has a high heat effect.

It is interesting to note that the cyclisation of allenes may be carried out on the same carbonylphosphinenickel catalysts. Benson and Lindsey[20] obtained the allene trimers (II) and (III) and the tetramer (IV) by heating allene at 105–110° in tetrahydrofuran in the presence of $[Ni(CO)_2\{P(OC_6H_5)_3\}_2]$ for 5–6 hours:



(II) (III) (IV)

The simultaneous cyclisation of allene and alkynes, which they also carried out, gave a mixture of isomeric dimethylenecyclohexenes.

Schrauzer showed that when acetylene reacts with acrylonitriles in the presence of $Ni(CO)_3(PPh_3)$, there is a considerable induction period[21]. This indicates that the true reaction catalyst is not $Ni(CO)_3(PPh_3)$. Actually, it has been shown that the reaction is more complicated:

$$Ni(CO)_3PPh_3 + 2CH_2{=}CH{-}CN \longrightarrow Ni(CH_2{=}CH{-}CN)_2 \cdot PPh_3 + 3CO.$$

In the presence of acetylene, complexes of nickel with acrylonitrile and acetylene are formed:

$$Ni(CH_2{=}CH{-}CN)_2(C_2H_2)_2 \quad \text{or} \quad Ni(CH_2{=}CH{-}CN)(C_2H_2)_2 \cdot PPh_3.$$

Similar nickel complexes were obtained with acrolein and fumaronitrile, etc.[22]

Under certain conditions the complex of $Ni(CH_2{=}CHCN)_2$ with alkyne derivatives forms aromatic nitriles (tetraphenylbenzonitrile with tolan) on decomposition, but with an excess of symmetrical alkyne hexasubstituted derivatives of benzene are formed. With acetylene itself in tetrahydrofuran under pressure, this complex gives cyclo-octatetraene and benzene. However, the yields are low, which indicates the non-catalytic nature of this synthesis. The introduction of triphenylphosphine into the complex sharply increases the yields of benzene (cyclo-octatetraene is not formed at all), and the process acquires a catalytic character[22].

2. Cyclotrimerisation in the Presence of Carbonyls of Other Metals

The carbonyls of a number of transition metals and their complexes with alkynes form another large group of active catalysts for the cyclic trimerisation of alkynes. In recent years, great successes have been achieved in the chemistry of (metal carbonyl)–alkyne complexes. This subject, which is of interest in itself, has been considered in detail in a recent review by Bennett[23]. Here it should be mentioned that in many of these complexes the component alkynes form cyclic aromatic structures.

Reppe established that when acetylene reacts under pressure with the hydrogen derivative of iron carbonyl, $Fe(CO)_4H_2$, a complex if formed, decomposition of which yields hydroquinone[24]. Later, Sternberg and coworkers reported the synthesis of an $Fe(CO)_3$–duroquinone complex from pentacarbonyliron and dimethylacetylene[25]. Hübel and coworkers prepared a large number of complexes of acetylene and its derivatives with the carbonyls of iron, manganese, tungsten, and cobalt[26]. These compounds are stable, and they may be regarded as π-complexes, constructed from an organic system and one or more metal-carbonyl groups. When the complex contains more than one alkyne molecule, a ring system with conjugated double bonds (frequently with one or two carbonyl groups in the ring) is formed within the complex. In no instance could the unchanged alkyne be recovered from the complex. Decomposition of such complexes as $[Fe(CO)_4 \cdot (Ph.C \vdots C.Ph)_2]$ or $[Fe_2(CO)_7 \cdot (Ph.C \vdots C.Ph)_2]$ and $[Fe(CO)_4 \cdot (HC \vdots CPh)_3]$ or $[Fe_2(CO)_6 \cdot (HC \vdots CPh)_3]$ gives the corresponding tetraphenylcyclopentadienone and 1,3,5-trimethylbenzene.

In subsequent papers by Hübel, it is shown that mono- and di-substituted acetylenes are converted in high yield into benzene derivatives in the presence of small quantities of some metal-carbonyl compounds[27]. The yield of trimer largely depends on the nature of the metal carbonyl. Table 1 gives information on the cyclic trimerisation of tolan with various metal-carbonyl catalysts(without solvent).

TABLE 1. Cyclic trimerisation of tolan without a solvent with various catalysts[27].

Carbonyl compound	Temperature, °C	Yield of trimer
$Fe_3(CO)_{12}$	260—280	75
$Fe_2(CO)_9$	250	25
$Fe(CO)_5$	270	20
$Fe_2(CO)_6\cdot(PhC{\equiv}CPh)_3$	270	60
$[Co(CO)_4]_2Hg$	270	70
$Co_2(CO)_8$	280	60
$Co_2(CO)_6\cdot(PhC{\equiv}CPh)_2$	150	70
$Ni(CO)_4$	260	5
$Mn_2(CO)_{10}$	270	55
$Mo(CO)_6$	270	50
$W(CO)_6$	270	15

It is more convenient to carry out the reaction in a solvent; the best cyclotrimerisation catalyst are then $Co_2(CO)_8$, $[Co(CO)_4]_2Hg$, $Co_2(CO)_6RC_2R'$ or $Co_4(CO)_{10}\cdot RC_2R'$, and dioxan is the best solvent. Table 2 gives information on the cyclotrimerisation of various alkynes with these catalysts.

Unsymmetrical alkynes are cyclised exclusively to 1,2,4-trisubstituted benzenes. Prop-2-yn-1-ol is readily cyclotrimerised by Reppe's catalyst, but all attempts to carry out the reaction in the presence of cobalt-carbonyl catalysts have been unsuccessful, as have been attempts to cyclotrimerise propargyl benzoate, propargyl acetate, and benzylacetylene. Hübel also carried out the simultaneous cyclotrimerisation of various alkynes — tolan with *pp'*-dichlorodiphenylacetylene or with phenylacetylene, and phenylacetylene with acetylene. The relative reactivity of alkynes in a given reaction can be determined by carrying out the simultaneous trimerisation of equimolecular quantities of the alkynes. When the reactivities are identical, all four possible products are obtained in the statistical ratio 1 : 3 : 3 : 1 (for example, in the simultaneous trimerisation of tolan with *pp'*-dichlorodiphenylacetylene).

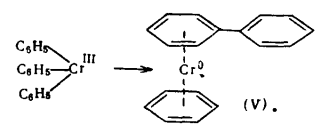
Cyclotrimerisation of alkynes in the presence of cobalt carbonyls was found to be a convenient method for the preparation of benzene derivatives containing bulky substituents. A derivative of benzene with an *ortho*-tertiary group — 1,2,4-tri-t-butylbenzene — was first obtained in this way[28]. The presence of adjacent t-butyl groups distorts the benzene ring; this is indicated by spectroscopic and thermochemical data[29]. Distortion of the benzene ring has also been noted in 1,2,4,5-tetra-t-butylbenzene, which was obtained later by a similar method[30]. It is interesting that the trimethylsilyl group does not produce this effect[29]. Cyclisation of di-isopropylacetylene in the presence of catalytic quantities of $Co_2(CO)_8$ gave hexaisopropylbenzene[31], in the molecule of which rotation of the isopropyl groups is hindered almost completely for steric reasons.

TABLE 2. Cyclic trimerisation of various alkynes with cobalt-carbonyl compounds.

Alkyne compound	Catalyst	Trimer	Temperature, °C	Yield, %
$C_6H_5C{\equiv}CH$	$[Co(CO)_4]_2Hg$	1,2,4-triphenylbenzene	101	70
$BrC_6H_4C{\equiv}CH$	»	1,2,4-tri-(*p*-bromophenyl)-benzene	101	65
$(CH_3)_3SiC{\equiv}CH$	$Co_2(CO)_6\cdot(CH_3)_3SiC_2H$	1,2,4-tris(trimethylsilyl)-benzene	90—100	55
$HOCH_2CH_2C{\equiv}CH$	$Co_2(CO)_6\cdot HOC_2H_4C_2H$	1,2,4-tri(hydroxyethyl)benzene	101	14
$CH_3OCH_2C{\equiv}CH$	$Co_2(CO)_6\cdot CH_3OCH_2C_2H$	1,2,4-tri(methoxymethyl)-benzene	101	17
$C_3H_7C{\equiv}CH$	$[Co(CO)_4]_2Hg$	1,2,4-tri-n-propylbenzene	101	11
$C_6H_5C{\equiv}CC_6H_5$	»	hexaphenylbenzene	101	90
$ClC_6H_4C{\equiv}CC_6H_4Cl$	»	hexa-(*p*-chlorophenyl)benzene	101	95
$CH_3OCOC{\equiv}CCOOCH_3$	»	hexa(methoxycarbonyl)-benzene	200	25
$C_2H_5C{\equiv}CC_2H_5$	»	hexaethylbenzene	101	75
$C_6H_5C{\equiv}CCOOH$	$Co_2(CO)_6\cdot C_6H_5C_2CO_2H$	3,5,6-triphenylbenzene-1,2,4-tricarboxylic acid	101	11
$C_6H_5C{\equiv}CCOOCH_3$	$[Co(CO)_4]_2Hg$	trimethyl 3,5,6-triphenyl-benzene-1,2,4-tricarboxylate	101	55
$C_6H_5C{\equiv}CCl$	»	1,2,4-trichloro-3,5,6-triphenyl-benzene	101	14
$C_6H_5C{\equiv}CCH_3$	»	1,2,4-trimethyl-3,5,6-triphenyl-benzene	101	90

3. Cyclotrimerisation under the Influence of Organometallic Catalysts

It was established comparatively recently that organochromium compounds obtained over 30 years ago by Hein[32] are active catalysts for the cyclisation of alkynes. Zeiss and coworkers showed that in tetrahydrofuran solution triphenylchromium forms an octahedral coordination complex with three molecules of tetrahydrofuran[33]. This complex is stable in the absence of oxygen and moisture. Removal of the tetrahydrofuran leads to the rapid conversion of the triphenylchromium into a bisarylchromium(0) complex(V):



(V).

The tetrahydrofuran ligands may be easily displaced by alkyne molecules, which undergo cyclisation with the formation of benzene and polynuclear aromatic derivatives[34]. Intermediate alkyne complexes of triphenylchromium have not been isolated. Organochromium compounds are very sensitive to the action of acid acetylene hydrogen, and monosubstituted acetylenes destroy the catalyst; for this reason, it can only be used for the cyclisation of disubstituted acetylenes.

The direction of the reaction depends on the stoichiometric ratio of alkyne to the catalyst and on the nature of the organic groups linked with chromium. Thus, in the cyclisation of but-2-yne in the presence of triphenylchromium, hexamethylbenzene or 1,2,3,4-tetramethylnaphthalene may be obtained as the main products, depending on the $(C_6H_5)_3Cr$: but-2-yne ratio; some bis(hexamethylbenzene)chromium(0) is also formed.

Table 3 shows that with all catalyst : monomer ratios the reaction products contain a naphthalene derivative. Bis(hexamethylbenzene)chromium(0) is only formed when there is a large excess of but-2-yne; it is similar in structure to ferrocene, is fairly stable, and does not catalyse the cyclic trimerisation of alkynes. If triethylchromium, or a triarylchromium with *ortho*-substituted

TABLE 3. Effect of the ratio of but-2-yne to catalyst on the yields of trimers[34].

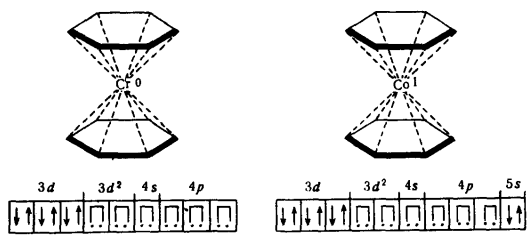
Molar ratio of $(C_6H_5)_3Cr$ to but-2-yne	1 : 1	1 : 2	1 : 3	1 : 5	1 : 20
Beginning of exothermic reaction, min	330	280	90	50	15
Yield of hexamethylbenzene, %	—	—	—	25	55
Yield of tetramethylnaphthalene, %	13	31	40	36	38

aryl groups (for example, trimesitylchromium), is used as catalyst instead of triphenylchromium, a benzene derivative is the sole reaction product.

The general character of this reaction was demonstrated by the formation of hexaphenylbenzene and 1,2,3,4-tetraphenylnaphthalene from tolan in the presence of triphenylchromium[34], and also by the formation of hexaphenylbenzene and 1,2,3,4-tetramethylphenanthrene from but-2-yne and tri-α-naphthylchromium.

Unlike chromium compounds, diphenylnickel does not react with alkynes to form naphthalene derivatives, but with tolan diethylnickel forms hexaphenylbenzene and 1,2,3,4-tetraphenylcyclohexa-1,3-diene, the latter being formed by the inclusion of the ethyl group of the catalyst in the ring[35,36].

The action of alkyl and aryl compounds of other transition metals, such as dimesityliron[37] or diphenylmanganese[38], also cyclises disubstituted acetylenes. In some respects diphenylcobalt(II) occupies a special position. Bis(hexamethylbenzene)cobalt(I), which is obtained by the reaction with but-2-yne, differs from the bisarene chromium derivatives by the presence of two electrons in excess of the complete krypton shell of the cobalt atom in this compound.



The capacity of cobalt to catalyse the reaction well outside stoichiometric proportions may be due to this special feature[38] (Table 4); in contrast, with the organochromium compounds, cyclisation occurs when the metal and the alkyne are present in stoichiometric proportions.

4. Cyclotrimerisation under the Influence of Complex Organometallic Catalysts

Ziegler's complex organometallic catalysts, which have been widely used in the polymerisation of alkenes and alkadienes, also polymerise alkynes. The polymerisation of acetylene and its homologues with the formation of linear high-molecular products was first carried out by Natta and coworkers[39]. Later, the results of more detailed study of the polymerisation of acetylene[40,41] and hexa-1-yne[42] were published. Because of the interesting properties of high-molecular alkyne polymers, a number of workers carried out the polymerisation of various alkynes in the presence of Ziegler-type[43-46] and other catalysts. Natta obtained the best results with catalysts of the type $AlR_3 + Ti(OR)_4$. Later, Hagihara and coworkers showed that with the catalytic system $Cr(t\text{-}OC_4H_9)_3 + Zn(C_2H_5)_2$ (ratio of components 1 : 3) monosubstituted acetylenes give linear dimers (vinylacetylene derivatives) in almost quantitative yield[47]. Replacement of diethylzinc by triethylaluminium led to the formation of alkylbenzenes. This shows how sensitive the alkyne polymerisation is to modifications in the catalytic system.

In 1959, Franzus and coworkers[48] first showed that cyclic trimers of disubstituted acetylenes (hexasubstituted benzenes) could be obtained with the aid of the catalytic system $Al(iso\text{-}C_4H_9)_3 + TiCl_4$; with an Al/Ti ratio within the range 1 : 1 to 3 : 1, dimethyl-, diethyl, and diphenyl-acetylene were quantitatively cyclotrimerised.

These workers note that none of the catalyst components alone catalyses cyclotrimerisation†. It was also shown that when $TiCl_4$ is replaced by $TiCl_3$ the catalytic system becomes inactive in this reaction.

Cyclic trimers of disubstituted acetylenes were also obtained by Wilke in presence of the $CrO_2Cl_2 + Al(C_2H_5)_3$ system[50]. Recently, Drefahl and coworkers made a very detailed study of the cyclotrimerisation of diphenylacetylene with Ziegler catalyst[51].

Although it was thought that monosubstituted acetylenes containing "acid" acetylene hydrogen would destroy the Ziegler catalyst, it was found that they also undergo the cyclotrimerisation reaction, forming 1,2,4- and 1,3,5-trisubstituted benzenes. A patent by Smith describes the use of a catalyst based on an organometallic compound of a non-transition metal and a transition metal halide[52]. A mixture of mesitylene (40%) and pseudocumene (60%) was obtained by the polymerisation of methylacetylene passed through a catalyst solution consisting of $Al(C_2H_5)_3$ and $TiCl_4$ in methylcyclohexane. The total yield of trimers exceeded 60%.

Lutz cyclotrimerised a number of mono- and di-substituted acetylenes in the presence of the $Al(C_2H_5)_3 + TiCl_4$ system (Table 5)[53]. He considers the use of large volumes of solvent to be the main condition for a successful synthesis. Reikhsfel'd and coworkers established that extensive dilution is not necessary, if the $Al(iso\text{-}C_4H_9)_3 + TiCl_4$ system is used as a catalyst[54]. 1,3,5-tri-n-butylbenzene was obtained from hex-1-yne, and 1,3,5-triphenylbenzene from phenylacetylene, in yields exceeding 90%. When this catalytic system is

TABLE 4. Cyclic polymerisation of but-2-yne on dimesitylcobalt[38].

But-2-yne, moles	6	8	10	20	40
$CoCl_2$, moles	1	1	1	1	1
Yield of hexamethylbenzene, % on Co	50	153	200	480	1000
Yield of π-complex, % on Co	20	20	20	20	20

TABLE 5. Cyclotrimerisation of alkynes in the presence of $Al(C_2H_5)_3 + TiCl_4$.[58]

Starting alkynes	Reaction temperature, °C	Trimers obtained	Yield, %	
			trimers	polymer
Acetylene	23—29	benzene	49.1	24.1
Methylacetylene	22—36	mesitylene	40.4	9.3
		pseudocumene	21.1	
Ethylacetylene	23—30	1,3,5-triethylbenzene	35.5	7.3
		1,2,4-triethylbenzene	17.0	
n-Butylacetylene	24—32	1,3,5-tributylbenzene	59.8	—
Dimethylacetylene	23—34	hexamethylbenzene	80.2	2.2
Diethylacetylene	24—32	hexaethylbenzene	76.5	—
Dibutylacetylene	86	hexabutylbenzene	52.2	4.6

† Under drastic conditions (pressure, temperature above 140°), Wilke obtained hexasubstituted benzenes from tolan and diethylacetylene by the action of di-isobutylaluminium hydride.

used, a change in the monomer : solvent ratio from 1 : 1 to 1 : 10 (1 : 20 according to Lutz) has no effect on the yield of trimer[55]. Replacement of $TiCl_4$ by $TiCl_3$ leads to the formation of extremely unsaturated polymers (rubber-like in the case of hex-1-yne), apparently of linear structure. Later, these workers carried out the simultaneous polymerisation of hex-1-yne and phenylacetylene[56]. With a 1 : 1 molar ratio of monomers all four possible trimers were obtained in amounts close to the statistical ratio (1 : 3 : 3 : 1). This distribution of products indicates that both alkynes have the same reactivity in the cyclotrimerisation.

A study of the effect of catalyst composition on the course of cyclotrimerisation showed that replacement of the transition metal halide in the $Al(iso\text{-}C_4H_9)_3 + TiCl_4$ system by an alkoxy-compound leads to a reduction in catalytic activity[57]; the use of tetraethoxytitanium completely deactivates the catalyst. Replacement of the alkyl group attached to aluminium by a chlorine atom has virtually no efect on the yield of cyclotrimerisation product.

Acetylenes with various substituents have been cyclotrimerised in the presence of a catalyst based on $Al(iso\text{-}C_4H_9)_3 + TiCl_4$; a number of alkynes have also been simultaneously cyclotrimerised with this catalyst[58] (Table 6).

Table 6 shows that propargyl bromide or 5-ethynyl-2-methylpyridine could not be cyclotrimerised; propargyl bromide attacks the catalyst. The direct cyclisation of t-butylacetylene was first carried out with the same catalyst, symmetrical as well as unsymmetrical isomers of tri-t-butylbenzene being obtained[59].

Hoover and coworkers used the $Al(iso\text{-}C_4H_9) + TiCl_4$ system for the cyclotrimerisation of vinylacetylene[60,61], and for the cotrimerisation of divinylacetylene and acetylene[61,62]. At -10°C vinylacetylene gave 1,2,4-trivinylbenzene in about 50% yield; when the temperature was raised to 30–50°, the yield decreased to 10%. Simultaneous cyclotrimerisation of divinylacetylene and acetylene gave *o*-divinylbenzene in 30% yield; when acetylene was replaced by methylacetylene, a mixture of trimethylbenzene isomers and dimethyl-*o*-divinylbenzene was formed. Trivinylbenzene is of interest as a cross-linking agent and as a monomer for the preparation of thermostable plastics used in rocket technology[63].

Donda and coworkers, who studied the cyclic trimerisation of phenylacetylene in the presence of $Al(C_2H_5)_3 + TiCl_4$, obtained 1,3,5- and 1,2,4-triphenylbenzene and a linear polymer[64]. The relative yields of cyclic and linear product depend mainly on the Al/Ti ratio. If this ratio was less than 4, linear polyphenylacetylene was not formed; the highest yield (75%) of aromatic compounds was obtained with an Al/Ti ratio of 2 to 4; the ratio of isomers is virtually independent of the Al/Ti ratio (60% 1,2,4-isomer and 40% 1,3,5-isomer). With higher Al/Ti ratios (4–7), the yield of benzenes fell sharply, and linear polymer was obtained as the main product. These workers point out that the solvent has an appreciable effect on the course of the reaction. The results given above refer to reactions in benzene; in heptane, with an Al/Ti ratio of unity, only oily linear polymers were obtained.

TABLE 6. Cyclotrimerisation of alkynes in the presence of $Al(iso\text{-}C_4H_9)_3 + TiCl_4$.[58]

Starting alkynes	Temperature, °C	Yield of products, %	
		cyclic	linear
Methylacetylene	20—40	60	traces
n-Butylacetylene	20—40	90	»
n-Octylacetylene	20—40	90	»
Phenylacetylene	20—40	90	»
Vinylacetylene*	0—10	37	10
Propargyl bromide	20	0	0
Furylacetylene	20—40	17.2	4.8
2-Methyl-5-ethynylpyridine	60	0	0
Triethylsilylacetylene	20—40	—	44
n-Butylacetylene + phenylacetylene	20—40	82.5	traces
n-Butylacetylene + triethylsilylacetylene	20—40	77	»
n-Butylacetylene + furylacetylene	20—40	28.5	2

* Catalyst $Al(iso\text{-}C_4H_9)_2Cl + TiCl_4$.

These workers also studied the cotrimerisation in the presence of $Al(C_2H_5)_3 + TiCl_4$ of acetylene and methylacetylene[65], and of acetylene with phenylacetylene and tolan[66]. As with pure phenylacetylene, the preferential formation of linear or cyclic polymers is determined by the Al/Ti ratio; the highest yields of aromatic trimers were obtained with an Al/Ti ratio of 3–4.

Dale used trimethylaluminium with $TiCl_4$ as a catalyst in the synthesis of 1,3,5-tris(trimethylsilyl)benzene from trimethylsilylacetylene[29]. The reaction was carried out at 60°, and a certain amount of the 1,2,4-isomer was obtained in addition to the 1,3,5-isomer.

Kambara and coworkers[67] studied the polymerisation of acetylene in the presence of various modifications of Ziegler catalyst; they noted that when one of the components of the catalytic system is a halogen derivative of a transition metal, a considerable quantity of benzene is formed with an increased degree of conversion of acetylene. Thus, with 43% acetylene conversion in the presence of $Al(C_2H_5)_3 + TiCl_4$ at 0°, 76% of the acetylene that reacts is converted into benzene. In all instances a linear polyacetylene is formed in addition to benzene; if a tetra-alkoxytitanium or a tetra-alkoxychromium is a component of the catalyst, the sole reaction product is a linear polyacetylene. Replacement of the titanium halide by VCl_4, $VOCl_3$, or VCl_3 leads to the exclusive formation of benzene, Starik and coworkers obtaining benzene from acetylene in up to 72% yield[68].

Recently, the results of a detailed study of the cyclisation of isopropenylacetylene in the presence of various catalytic systems was published[69]. The highest yield of cyclic products (1,3,5- and 1,2,4-tri-isopropenylbenzenes) was obtained with the catalyst $Al(C_2H_5)_3 + TiCl_4$. A change in the nature of the transition metal in the catalyst was reflected both in the tendency to form cyclic trimers and in the ratios of the isomeric cyclisation products. The ratio of 1,3,5- to 1,2,4-isomers decreased with the transition from titanium to cobalt and increased slightly with the use of nickel compounds.

5. Cyclotrimerisation in the Presence of Other Catalysts

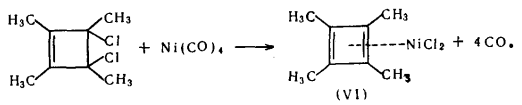
Other catalysts have also been proposed for the cyclic trimerisation of alkynes. Blomquist and Maitlis[70] found that in solvents containing no hydroxyl groups (benzene, acetone, chloroform) the complex bis(benzonitrile)palladium chloride catalyses the cyclotrimerisation of tolan in hexaphenylbenzene with a yield of 85%. The use of catalysts based on CrO_3 on aluminosilicate[71], and gel-like oxides (for example, $SiO_2 + Al_2O_3$) surface-treated with diborane[72], for the cyclisation of alkynes is described in the patent literature. Hexaphenylbenzene was obtained in

about 10% yield by the reaction of tolan with bromophenylmagnesium in a mixture of tetrahydrofuran and xylene[73]. Aromatic hydrocarbons were also obtained from acetylene derivatives by reaction of the latter with lead tetra-acetate in the dark[74].

Luttinger proposed an interesting catalytic system suitable for both the cyclisation and polymerisation of acetylenes[75]: this consists of a compound of a Group VIII metal and a hydride reducing agent; iron and metals not belonging to Group VIII are inactive. Alkali hydrides and silanes were used as reducing agents. The alkali tetrahydroborates and alkali tetrahydroaluminates were found to be the best agents. Hept-1-yne gives mainly linear polymers (dimers, trimers, and somewhat higher polymers), but other alkynes (phenylacetylene) also form aromatic products, such as 1,3,5- and 1,2,4-substituted benzenes[76]. The highest yield of benzene derivatives is obtained by the use of cobalt salts; the valence state of the metal (Co^{2+} or Co^{3+}) has no effect on the process. The usual catalyst for linear polymerisation is $NiCl_2 + NaBH_4$.

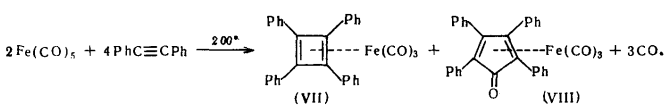
III. SYNTHESES OF NON-BENZENOID CYCLIC STRUCTURES

Under certain conditions, derivatives of cyclobutadiene, which is of great theoretical interest, may be obtained from alkynes. A compound containing the cyclobutadiene ring (VI) was first obtained by Schröder and Criegee according to the reaction[77]:



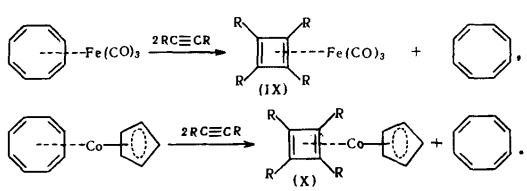
(VI)

Complex formation with compounds of a transition metal stabilises the cyclobutadiene ring. In recent years, complexes of cyclobutadiene derivatives with compounds of Fe, Co, Ag, and Pd have been obtained. Hübel and Braye[78] have reported on the reaction between $Fe(CO)_5$ and tolan, in which the tetraphenylcyclobutadiene complex (VII) is obtained in addition to other products[78]:



(VII) (VIII)

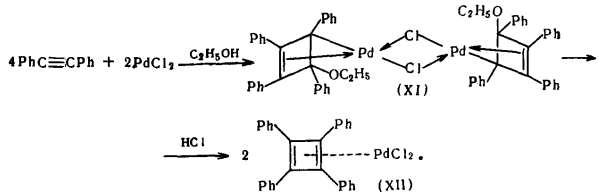
Dodge and Schomaker proved the structure of this complex from X-ray analysis[79]. Nakamura and Hagihara synthesised the same complex by the reaction of tricarbonylcyclo-octatetraeneiron with tolan[80]. Using an analogous reaction, they also synthesised the cobalt complex containing the cyclobutadiene ring (X):



(IX) (X)

Both these complexes are stable in air and they are very thermostable, being unchanged under nitrogen up to 360°; in this way they are to a certain degree reminiscent of ferrocene. Strong acids and alkalis have no action on them.

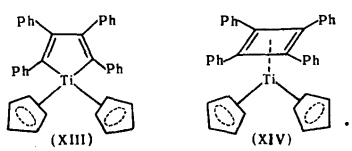
Malatesta and coworkers obtained a similar compound by the reaction of tolan with a solution of palladium(II) chloride in ethanol, with subsequent decomposition by hydrochloric acid[81]:



(XI) (XII)

Blomquist[70] confirmed Malatesta's results; by treating tolan with palladium(II) chloride in a mixture of ethanol and chloroform, he obtained the complex (XI) in 83% yield, and by passing gaseous hydrogen chloride through a solution of this in chloroform, he obtained the complex (XII) in 76% yield. The infrared and NMR spectra of the latter are very similar to the spectra of the complex of $NiBr_2$ with tetraphenylcyclobutadiene.

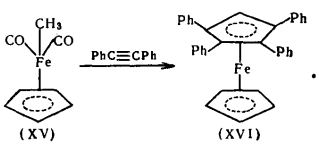
By the reaction of tolan with titanocene, Vol'pin and coworkers[82] obtained the compound π-$(C_5H_5)_2Ti(PhC{\equiv}CPh)_2$, to which structure (XIII) was assigned. Since the properties of the compound obtained are very reminiscent (stability of the pure compound and its benzene solutions, etc.) of the complexes of iron and cobalt with tetraphenylcyclobutadiene previously described, and since the electron configuration of the valence shell of the titanium atom in cyclobutadienebis(cyclopentadienyl)titanium (XIV) is similar to the inert gas configuration (like X), the compound obtained by Vol'pin and coworkers appears to have the structure (XIV):



(XIII) (XIV)

Five-membered rings may also be formed in the cyclisation of alkynes. In the cyclisation of disubstituted acetylenes in the presence of metal carbonyl catalysts, tetrasubstituted cyclopentadienones are often obtained in addition to benzene derivatives[26,31,78,83,84]. These are formed by the union of two molecules of acetylene with one of the carbonyl groups of the catalyst. As a rule, the cyclopentadiene ring formed remains in the metal carbonyl complex as an organic ligand.

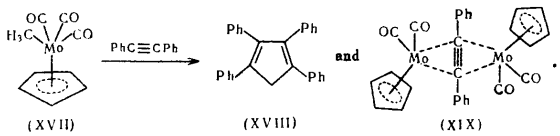
Nakamura observed an interesting reaction between carbonylcyclopentadienylalkyls of iron and molybdenum with alkynes[85]. Thus, toluene reacted with π-$C_5H_5FeCH_3$. $(CO)_2$ (XV) to give tetraphenylferrocene (XVI):



(XV) (XVI)

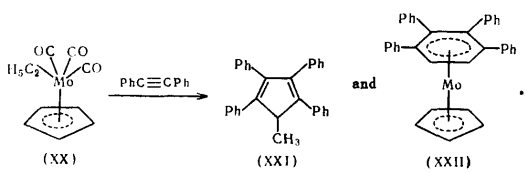
In this reaction the methyl group, which is initially linked to the iron atom, forms a cyclopentadienyl ring with two molecules of tolan. As would be expected, when tolan was replaced by acetylene, ferrocene was obtained. Ethyl and benzyl derivatives of iron carbonyl form benzene, and not ferrocene.

Cyclopentadienyl(methyl)tricarbonylmolybdenum (XVII) reacts with tolan to form tetraphenylpentadiene (XVIII) and the tolan complex (XIX), but the corresponding ethyl derivative (XX) reacts with tolan in a still more unusual manner:



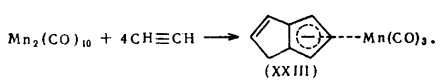
(XVII) (XVIII) (XIX)

In addition to other products, methyltetraphenylcyclopentadiene (XXI) and the "sandwich" compound cyclopentadienyl-(1,2,3,4-tetraphenylbenzene)molybdenum (XXII) are obtained, that is, in one reaction the ethyl group participates differently in the formation of a ring:



(XX) (XXI) (XXII)

Coffild and coworkers observed an unusual reaction[86]: when acetylene reacted with $Mn_2(CO)_{10}$ in tetrahydrofuran at 150° and 43 atm for 5 hours, a compound identified as tricarbonyl-π-dehydropentalenylmanganese (XXIII) was obtained:



(XXIII)

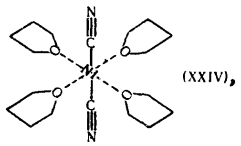
Rings containing eight and more carbon atoms may be obtained from acetylene and its derivatives. The work of Reppe[2] made an accessible one-stage synthesis of cyclo-octatetraene from acetylene possible, other cyclic higher polyalkenes being obtained at the same time in lesser quantities[2]. It is unnecessary to present well known information on the preparation of cyclo-octatetraene here; we shall merely point out that Reppe used compounds of bivalent nickel as catalysts. Later, Schrauzer showed that cyclo-octatetraene can be obtained in stoichiometric quantities by the reaction of acetylene with organic complexes of zerovalent nickel, and benzene is always obtained at the same time[22].

IV. MECHANISM OF CYCLISATION OF ALKYNES

It is generally considered that the formation of a benzene ring by the thermal cyclisation of acetylene proceeds by two successive bimolecular reactions through an intermediate stage in which vinylacetylene or its derivatives is formed[1].

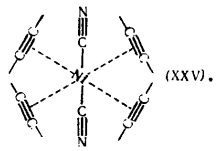
Reppe was the first to propose an explanation of the mechanism of formation of cyclo-octatetraene in the presence of catalysts[2]. According to his interpretation, the effective catalysts are unstable nickel–acetylene compounds obtained by the action of acetylene on the initial nickel compounds (for example, halides); the unstable nickel acetylide, or the metal itself, adds new molecules in such a way that 4 molecules of acetylene are arranged in coordination around the Ni^{2+} ion. This complex decomposes by way of a hypothetical intermediate biradical of four acetylene molecules to form cyclo-octatetraene and nickel compounds.

McKinley has discussed this problem in greater detail[87]. He suggests that the catalyst, for example, nickel cyanide, forms a coordination complex of type (XXIV) with tetrahydrofuran:



(XXIV),

in which four molecules of tetrahydrofuran lie in the same plane as the nickel atom, and the CN group is arranged perpendicular to this plane. Acetylene readily displaces tetrahydrofuran to give a new complex (XXV):

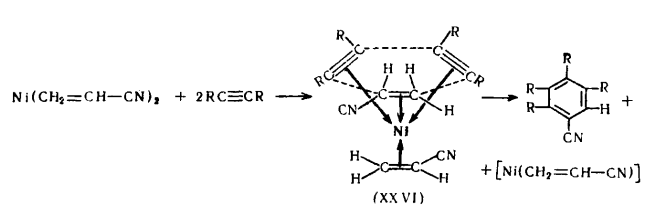


(XXV).

Since the carbon atoms of adjacent molecules are situated close to one another, it may be supposed that the electrons of the triple bond which make the bond with nickel are redistributed with the formation of simple covalent C–C bonds. The formation of octamethylcyclo-octatetraene from dimethylacetylene[87] proves that the acetylene hydrogen does not play a part in the reaction and that the metal is directly linked to the triple bond of the acetylenes. McKinley explains the exclusive capacity of nickel compounds to catalyse the synthesis of cyclo-octatetraene by favourable steric conditions for the formation of the acetylene complex, which is confirmed by the construction of Stuart–Briegleb models[87].

These ideas have been developed by Schrauzer from a more modern point of view[22,88,90]. He assumes that cyclisation reactions proceed inside metal–alkyne complexes by many-centred reactions. The first step must be considered the formation of π-complexes of the metal with the alkynes, in which a new compound is then formed on the basis of spatial proximity and geometrical arrangement. The structure of the reaction product would then be expected to depend on the structure of the π-complex transition state; this has been confirmed by experiments with bis(acrylonitrile)nickel(0)[22]. Such a complex could unite with two alkyne molecules. Since nickel here has zero valency, the complex retains the tetrahedral configuration. In the π-complex (XXVI), two molecules of alkyne are approximately coplanar with one nitrile molecule.

As would be expected, the final reaction product is benzonitrile. Under certain conditions one of the two nitrile molecules may also be displaced by an alkyne molecule with the formation of a benzene derivative.



(XXVI)

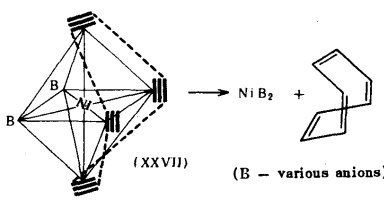
The addition of such an active electron donor as triphenylphosphine to bis(acrylonitrile)nickel(0) increases the

catalytic activity of the nickel compound in the acetylene cyclisation reaction by a factor of 100. Benzene is then the main product of the reaction.

Schrauzer and Eichler made a detailed study of the synthesis of cyclo-octatetraene on a typical catalyst, consisting of bivalent nickel with weak anion bonds, or — in the terms of modern coordination theory — with a weak ligand field[88]. They established a relationship between the structure of the complex and its magnetic properties on the one hand, and its activity in the cyclisation reaction on the other hand (Table 7).

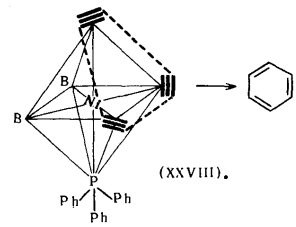
The relationship between the lability of the ligands and the catalyst activity was demonstrated in the synthesis of cyclo-octatetraene in the presence of bis(salicylaldiminato)nickel(II) and its *N*-alkyl derivatives; the methyl derivative, which is the most labile, was also found to be the most active.

Complexes with an octahedral configuration are active. The Ni^{II} ion "solvated" by acetylene molecules remains paramagnetic, because the ligand field strength (of acetylene) is insufficient for the pairing of spins of both split nickel electrons. The acetylene molecules will attempt to occupy a suitable octahedral configuration around the central field. Hence, Schrauzer and Eichler assume that the transition state in the formation of cyclo-octatetraene is a complex with four acetylene molecules with a steric arrangement suitable for the synthesis of cyclo-octatetraene (XXVII). Intermediate stages are not necessary for these molecules to form a ring:



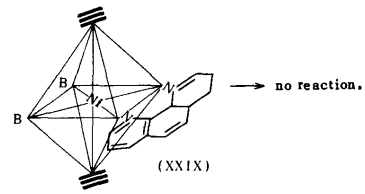
(XXVII) (B — various anions).

Experiments on the inhibition of cyclisation favour the hypothesis that cyclo-octatetraene is formed in labile acetylene complexes with an octahedral, or closely related, structure on the Ni^{II} ion[88]. Donor molecules with a strong ligand field were used as inhibitors. The addition of triphenylphosphine inhibits the formation of cyclo-octatetraene; the reaction proceeds with a tendency to form benzene, which is obviously related to blocking of one of the coordination positions in the complex (XXVIII) by a PPh_3 molecule:



(XXVIII).

The addition of compounds capable of blocking two coordination positions in the complex (*o*-phenanthroline) at once completely deactivates the catalyst:



(XXIX)

Schrauzer put forward the idea that a π-complex many-centre reaction occurs in this and similar instances. The rehybridisation of the acetylene carbon atoms from the sp- and sp^2-states, necessary for the formation of new C–C bonds, is obviously greatly facilitated by the formation of a π-complex with a transition-metal atom. The subsequent reaction of the rehybridised atom is, as a rule, not specific. Thus, with alkynes $Fe_2(CO)_{12}$ gives a large number of different organometallic complexes and organic compounds at the same time[26,27]. According to Schrauzer, nickel compounds, in contrast to compounds of other elements, can catalyse the formation of cyclo-octatetraene from acetylene, because of the difference in the energies of states in the interaction of the metal used and acetylene. In the active complexes the $3d$-terms for Ni^{II} lie in a region which favours the formation of labile compounds with acetylene molecules of just the required size. The Ni-ligand bond in these complexes shows a relatively high degree of covalency; the Ni^{II} ion carries only a weak positive charge, and therefore the energy of the $3d$-state approaches so closely to the energy of the π_g-orbitals of the acetylenes that weak dative bonds may even be formed. (In the more polar and catalytically inactive nickel halides, the energy difference between the corresponding orbitals is too great for any kind of interaction to occur between them). Analogous complexes of Co, Fe and other metals obviously do not satisfy this requirement.

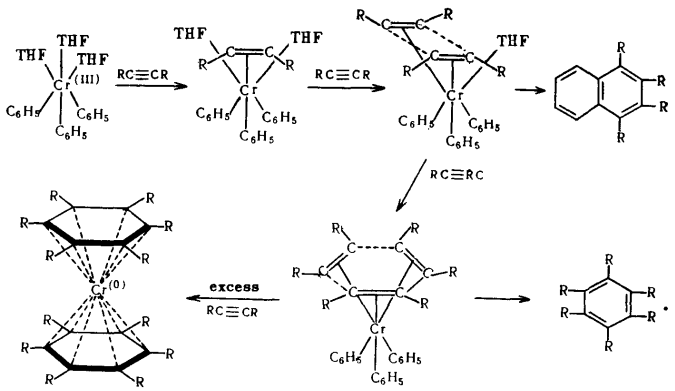
According to Schrauzer, the hypothesis previously proposed that cyclo-octatetraene results from dimerisation of cyclobutadiene, formed as an intermediate, is unsound[89]. It would be difficult to understand why catalytic quantities of cyclobutadiene produced in the presence of a large excess of acetylene would be selectively converted into cyclo-octatetraene and only give benzene in the presence of triphenylphosphine. Moreover, in its electronic structure cyclobutadiene belongs to the class of strong π-bonded ligands. The nickel complex of cyclobutadiene would therefore be more stable kinetically than the initial complex. The rate of conversion of such a complex into cyclo-octatetraene would then be the determining factor, which is not in agreement with the experimental results[90].

However, the idea of the formation of cyclobutadiene as an intermediate permits the interpretation of results on

TABLE 7. Classification of catalysts for the synthesis of cyclo-octatetraene.

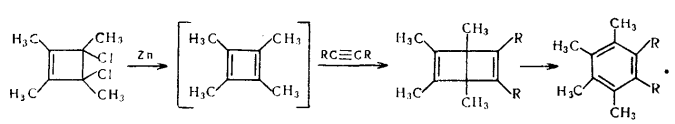
	Weak ligand field	Intermediate range	Strong ligand field
Configuration	octahedral	octahedral and planar	planar
Magnetic behaviour	paramagnetic	anomalously magnetic	diamagnetic
Exchange of ligands	rapid	moderately rapid	very slow
Catalytic activity	active	active	inactive
Examples	bis(salicylaldehydato)nickel bis(acetylacetonato)-nickel	nickel cyanide bis-(*N*-alkylsalicylaldiminato)nickel	nickel phthalocyanine bis(dimethylglyoximato)nickel

the cyclisation of alkynes in the presence of the alkyl- and aryl-metal catalysts of Zeiss[34]. The proposed mechanism is represented by the following scheme:



It is assumed that the alkyne molecules progressively displace the tetrahydrofuran ligands, the octahedral configuration of the complex being retained. The phenyl groups linked to chromium may take part in the reaction with an entering alkyne molecule. Although intermediate complexes with one, two, or three alkyne molecules have not been separated, under certain conditions products of the reaction of an acetylene molecule with one or two phenyl groups of triphenylchromium have been obtained; these are derivatives of styrene or stilbene[91]. But generally the displacement of tetrahydrofuran molecules goes further. As has already been mentioned, the products of the reaction of alkynes with triphenylchromium always contain naphthalene derivatives. According to Zeiss, this indicates the formation of an extremely reactive intermediate, tetra-alkylcyclobutadiene, in the chromium coordination sphere. The chromium atom in the complex can catalyse the elimination of hydrogen in the *ortho*-position of a phenyl group linked to it; dehydrobenzene is then obtained, which reacts with the tetra-alkylcyclobutadiene by an unusual intramolecular Diels–Alder reaction with the formation of tetra-alkylnaphthalene. When the reaction mixture contains sufficient alkyne, the tetra-alkylcyclobutadiene complex of triphenylchromium either loses the last molecule of tetrahydrofuran, which is replaced by alkyne, or it gives a hexa-alkylbenzene by an intermolecular Diels–Alder reaction. With a large excess of alkyne, small quantities of a bis(arene) complex are obtained as the product of further replacement of groups initially linked with chromium. When the *ortho*-position of the phenyl groups is occupied, for example, in trimesitylchromium, naphthalene derivatives are not formed.

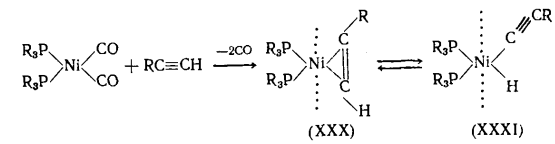
Results obtained by other workers also indicate that the cyclobutadiene ring may be formed in the cyclisation of alkynes. Berkoff and coworkers reduced 1,2,3,4-tetramethylcyclobutene in but-2-yne or dimethyl butynedioate and obtained hexamethylbenzene and dimethyl tetramethylphthalate respectively[92]. They suggest the following scheme for the reaction:



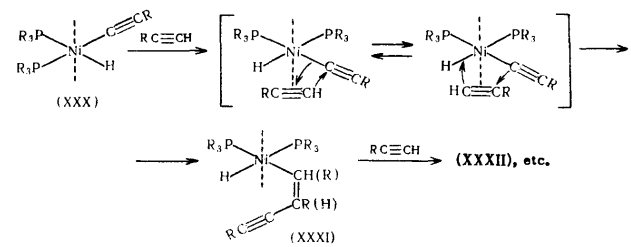
In the cyclisation of di-isopropylacetylene, Arnett and coworkers obtained, in addition to benzene and cyclopentadiene derivatives, products the formation of which is difficult to explain without the hypothesis that cyclobutadiene is produced as an intermediate[31].

Meriwether has put forward quite different interpretations on the mechanism of alkyne polymerisation and cyclisation with nickelphosphinecarbonyl catalysts[19]. Assuming the initial formation of a π-complex, he considers that the subsequent polymerisation or cyclisation steps occur with the participation of an organonickel compound having a metal–carbon σ-bond.

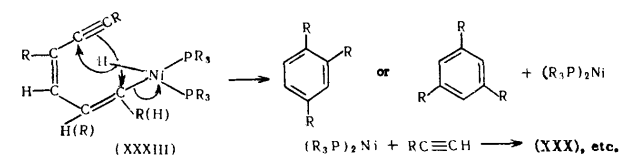
According to Meriwether, the Ni–phosphineacetylene complex obtained by replacement of carbonyl groups by acetylene molecules (XXX) is an "active" catalyst. The complex (XXX) is similar in structure to the biphosphine–Pt–acetylene complexes prepared by Chatt and coworkers[93]:



The complex (XXXI) is an active catalyst for both linear polymerisation and cyclisation. Both complexes are planar and the nickel in them has a formal valency of +2, that is, the nickel atom has a vacant p_z-orbital capable of forming π-bonds with a second acetylene molecule:

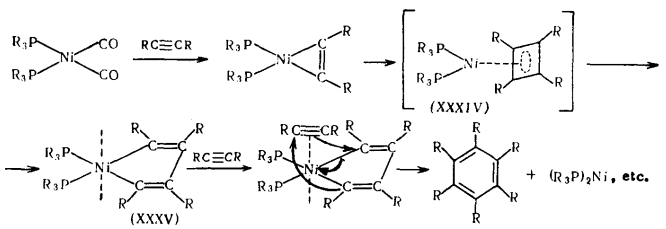


When the complex (XXXIII) has a favourable conformation, in which the first and sixth atoms of the carbon chain can approach within bonding distance, simultaneous hydrogen transfer and ring closure leads to the formation of the corresponding aromatic products:



This mechanism is not applicable to disubstituted acetylenes, since transfer of an acetylene hydrogen is its characteristic feature. Meriwether was therefore compelled to give another explanation of the polymerisation of disubstituted acetylenes. The initial type (XXX) complex formed reacts with a second acetylene molecule and, after the intermediate formation of diphosphinecyclobutadiene-nickel (XXXIV), gives a planar complex (XXXV); in this

planar complex, Ni^{2*} has a vacant *pz*-orbital and is capable of coordinating with a third acetylene molecule:

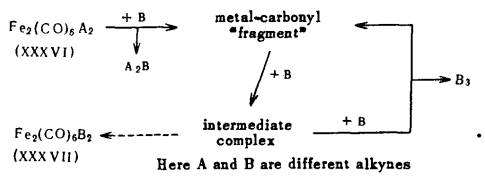


Meriwether points out that acetylene and monosubstituted acetylenes may be partly or completely polymerised by this mechanism. Meriwether's mechanism for the cyclisation of acetylenes is very artificial. This accepted scheme requires two different mechanisms for mono- and di-substituted acetylenes, which makes it doubtful.

The evidence presented in recent years that compounds of nickel with cyclobutadiene can add donor molecules (for example, the addition of triphenylphosphine or *o*-phenanthroline to tetramethylcyclobutadienenickel dichloride[94]) makes Meriwether's objection to the activation of a third acetylene molecule by the complex (XXXIV) unconvincing.

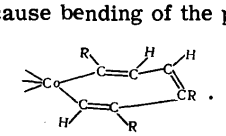
Nakamura has proposed a mechanism for the cyclisation of acetylenes which is somewhat similar to that given above; it also requires the formation of a heterocyclic compound with the metal in the ring[85].

Hübel considers that the catalytic action of metal carbonyls and their derivatives is explained by the formation of active "fragments"[27]. It is significant that the polynuclear compounds of iron and cobalt are the most active compounds. If the reaction with alkynes is carried out under conditions that exclude the formation of metal-carbonyl "fragments" (for example, with carbon monoxide under pressure), trimerisation does not occur. The following scheme is suggested:



Here A and B are different alkynes

The complex (XXXVI) reacts to only a slight degree with B, metal-carbonyl "fragments" being formed in addition to the trimer A_2B. These "fragments" react with B by way of an intermediate complex to form the trimer B_3 and new "fragments". The stable complex (XXXVII) is formed in a side-reaction. The proposed structure for the intermediate complex, for example, in the cyclotrimerisation of t-butylacetylene to 1,2,4-tri-t-butylbenzene[28], includes a non-planar seven-membered ring(bulky groups in *ortho*-positions cause bending of the plane of the ring):

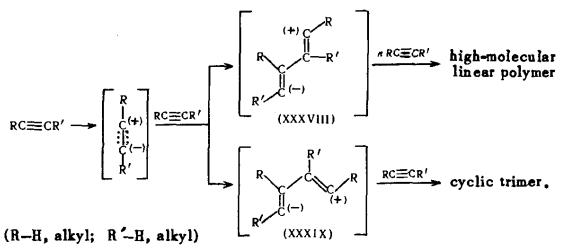


Because the ring is not planar, steric hindrance is eliminated. A benzene compound is not formed in the complex itself; this is proved by the formation of aliphatic oils when the complex is hydrogenated. The aromatic ring is closed only when the complex is decomposed (in this case, for example, by the action of bromine).

The existence of heterocyclic structures containing a metal in complexes of this kind has not been confirmed by results obtained later[95], according to which alkyne molecules in the complex can be replaced relatively easily by molecules of another alkyne present in solution. This exchange is much more probable for metal-alkyne π-complexes than for ring structures not containing triple bonds.

Ziegler's catalysts are amongst the most active in the cyclisation of alkynes. In one of the first papers in this field[53], Lutz attempted to explain the mechanism of the catalytic action of the $Al(C_2H_5)_3$–$TiCl_4$ system. Since a certain amount of linear polymers is usually obtained, according to Lutz the direction of the reaction depends on the suitability of the particular conformation of the intermediate complex. With disubstituted acetylenes, the confirmation that determines subsequent cyclisation is sterically favourable; with monosubstituted acetylenes, the probability of this route increases with the mass of the substituent.

According to Lutz, the polymerisation of alkynes is a surface-catalytic process, chain growth being effected through Al–C bonds formed by chemisorption of the alkynes on the catalyst.

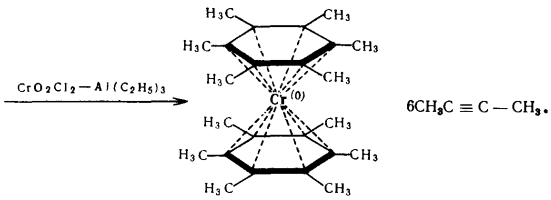


A polarised intermediate compound is formed on the catalyst, and this can react with adjacent polarised molecules by one mechanism or the other. The high selectivity shown in the cyclisation of disubstituted acetylenes indicates the importance of steric factors; steric hindrance interferes with the formation of the intermediate (XXXVIII). Even if it were formed, attack of the active end of the growing chain would be completely blocked by alkyl groups. Lutz has not solved the problem of the cyclisation of monosubstituted acetylenes. Lutz's scheme does not accomodate the catalytic system AlR_3–$TiCl_3$, which is known to have a solid surface; * this, however, promotes linear polymerisation[54], that is, according to Lutz's scheme, a less probable reaction.

It is interesting to consider Wilke's point of view on the mechanism of butadiene cyclotrimerisation[96]. As is well known, when this reaction was carried out in the presence of Ziegler-type catalysts, cyclododeca-1,5,9--triene was obtained. According to Wilke, the process comprises three steps: (1) the formation of a π-complex of butadiene with a transition metal, (2) the formation of new C–C bonds of preoriented molecules with the production of a ring, and (3) separation of the cyclic trimer, or its displacement by new butadiene molecules.

This scheme has been confirmed by experiments on the cyclisation of but-2-yne with the catalytic system CrO_2Cl_2–$Al(C_2H_5)_3$, which, like $TiCl_4$–$Al(C_2H_5)Cl$, promotes the cyclotrimerisation of butadiene[96]. The "sandwich" compound bis(hexamethylbenzene)chromium(0), which is generally obtained in the presence of Zeiss arylchromium

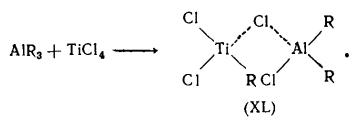
catalysts, was shown to be present in the reaction products.



This is further evidence that similar mechanisms must operate in the cyclisation of alkynes by different catalysts. Specificity in the activity of a given catalyst is determined by the nature of the metal and of the groups linked to it, and also by the reaction conditions. A general feature of all catalysts is the formation of a coordination-complex bond between the π-orbitals of the alkyne and the d-orbitals of the transition metal, together with redistribution of electrons and the formation of new C–C bonds. As Schrauzer has emphasised[88], the formation of new bonds is a non-specific reaction and nearly always occurs when an alkyne carbon atom can be brought within the sphere of action of a given transition-metal atom.

Ziegler's catalysts are no exception. On the basis of their own experiments and published results, the authors of the present review have put forward an interpretation of the mechanism of cyclotrimerisation on these catalysts[57]. Experimental results (identical course of the reaction in various solvents, identical reactivity in this reaction of acetylenes with substituents having an opposite effect on the electron density of the triple bond, etc.) suggest that the anionic mechanism usually postulated for polymerisation with Ziegler's catalysts is inapplicable. A coordination mechanism is more probable for the cyclotrimerisation of alkynes.

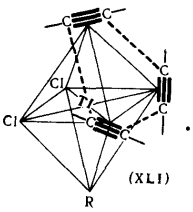
When the components of the catalytic system (for example, alkylaluminium and titanium halide) react, an active complex (XL) is formed:



(XL)

In this complex titanium is partly alkylated. The role of the alkylaluminium consists in the alkylation of titanium and the conferring of a formal charge on it. This is of great importance for the catalytic activity of the complex in cyclotrimerisation, since there is then a partial trans-hybridisation of the titanium valence electrons from the d^3s- to the sp^3-state[38]. According to the calculations of Pilcher and Skinner[97], trans-hybridisation promotes the formation of a simpler bond. It may be supposed that the main factor is the setting free in the $d^3s \rightarrow sp^3$ transition of the titanium d-orbitals, which may be used for interaction with the π-electrons of the triple bond.

The complex (XL) is highly polarised; in some papers even the possibility of the ionisation of such compounds has been considered[98–100]. It is very probable that under the reaction conditions the formation of the cyclic trimer is due to a "fragment" (an ion in the limiting case) $[TiRCl_2]$ which retains the tetrahedral configuration characteristic of both d^3s- and sp^3-hybridisation, but with one unoccupied apex. Since in the higher oxidation stages titanium has the coordination number six, the titanium atom can bind three molecules of acetylene in its coordination sphere:



(XLI)

The complex (XLI) assumes an octahedral, or close to octahedral, configuration, three molecules of acetylene being arranged approximately in the same plane. Such an arrangement facilitates the subsequent combination of the three acetylene molecules to form a ring. As Schrauzer points out[88], the transhybridisation of the alkyne carbon atoms from the sp- to the sp^2-state required for this is facilitated by the presence of a π-complex bond with the central metal atom. The benzene molecule formed in this way is very loosely bound to the remaining part of the complex and is easily displaced by new alkyne molecules. Cyclotrimerisation proceeds as a many-centred π-complex reaction (according to Schrauzer's classification). This is the most probable mechanism for the cyclisation of alkynes; however, the intermediate formation of a cyclobutadiene ring from two acetylene molecules in the coordination sphere of titanium is also possible. Because of experimental difficulties, information has not yet been obtained on the kinetics of cyclotrimerisation, which would provide a more definite answer to this question.

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After the manuscript of this review has been submitted for publication, further reports on the cyclisation of alkynes appeared, the most interesting of which will be briefly presented here.

New catalysts for cyclotrimerisation proposed in a number of patents include: $TiCl_4$–$LiAl(C_7H_{15})_4$ and $VOCl_3$–$Al(C_3H_7)_3$[101], compounds of the bis(trialkylphosphite)nickel(0) type[102], $NbCl_5$ and $TaCl_5$[103]. Reports have been made on a detailed investigation of the cyclisation of isopropenylacetylene in the presence of Ziegler's catalyst[104], on the preparation of hexaisopropenylbenzene (a nonreactive trimer of diisopropenylacetylene)[105], the radiochemical cyclisation of methyl- and phenyl-acetylenes[106], the cyclotrimerisation of 2-methylbut-3-yn-2-ol[107], and on the synthesis in the presence of Ziegler's catalyst of [^{14}C]benzene and [$^2H_6$]benzene[108] and of trimethylbenzenes from methylacetylene for the purpose of radiocarbon analysis[109]. A number of trialkynylbenzenes were obtained by the cyclisation in the presence of cobalt carbonyls of conjugated alkadiynes in which hydrogen at the triple bond is replaced[110]. The reactions of alkadiynes and cycloalkadiynes in the presence of Ziegler's catalysts and cobalt carbonyls have been studied[111]. In nearly all instances cyclic trimers and dimers were obtained in addition to polymers. $CoCl_2$ and $(C_2H_5)_2Al$(butynyl) were observed to react in an unusual manner[112]; the reaction products included benzene, the presence of which can be explained by the elimination of but-1-yne followed by its cyclotrimerisation and dealkylation of the trimer.

Some reports deal with the preparation from alkynes of cyclobutadiene complexes of Pd[113,114], Mo, W, Co[115], and

of complexes of transition metals containing the cyclopentadienone[116] and the tropone[117] ring. When perfluorobut-2-yne reacted with π-$C_5H_5Rh(CO)_2$, π-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium was obtained[118]; a study of the structure of this compound showed that only four atoms of the benzene ring are coordinated with rhodium, that is, the structure is not planar.

The addition of alkynes to cyclobutadiene derivatives[119] has been proposed as a method for the preparation of "Dewar" benzene[120]. It should be noted that great progress in the chemistry of valence isomers of benzene with non-classical Ladenburg and Dewar structures became possible when cyclic trimers of such compounds as t-butylacetylene and its derivatives had been prepared.

The observations of Schrauzer, which lead us to re-examine the mechanism of cyclisation, are of considerable interest[121]. In the reactions of alkynes in the presence of various compounds of Ni, Fe, Co, Mn and Pd, signals with a g-factor of ~ 2.0028 were obtained when the viscosity of the reaction medium was sufficiently high. The available information is not sufficient to enable a judgement to be made on the nature and role of this effect.

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COMPOUNDS OF THE β-TETRALONE SERIES

V.F.Shner and N.M.Przhiyaglovskaya

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I. INTRODUCTION

β-Tetralone — tetralone-2 [name used throughout in Russian text (Ed. of Translation)], or 3,4-dihydro-1*H*--naphthalen-2-one, or 1,2,3,4-tetrahydro-2-oxonaphthalene — and its derivatives are characterised by high reactivity and can be used for the synthesis of various compounds. Interest in them heightened after Robinson showed that they could serve as raw materials for the synthesis of steroids and terpenes. Subsequently β-tetralone was successfully used for the synthesis of compounds similar to morphine and chrysene derivatives.

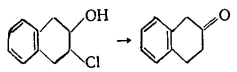
In several instances the interest lies not so much in β-tetralone itself as in various of its derivatives.

The problems of the synthesis of β-tetralone and its substituted derivatives and also the use of β-tetralone in syntheses have not been systematically covered in the

literature. The present review aims at a complete picture of work in the field of the chemistry of the compounds of the β-tetralone series.

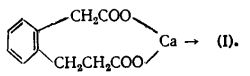
II. METHODS FOR OBTAINING COMPOUNDS OF THE β-TETRALONE SERIES

β-Tetralone (I) was first obtained in 1893 by Bamberger and Lodter [1] by the action of alkali at high temperature on 3-chloro-1,2,3,4-tetrahydro-2-naphthol. The yield of the product was somewhat increased on using quinoline or magnesium carbonate [2,3]:



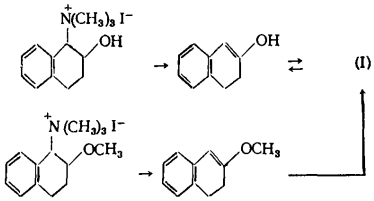
(I)

Somewhat later Einhorn and Lumsden [4] showed that β-tetralone is formed in the dry distillation of calcium 2-(carboxylatomethyl)phenylpropionate:

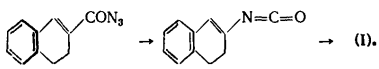


Soviet investigators [5-7] obtained β-tetralone by pyrolysis of 2-carboxymethylphenylpropionic anhydride and by Dieckmann condensation of the diethyl ester of the acid. However, their attempts to synthesise β-tetralone derivatives substituted in the aromatic nucleus by this method were unsuccessful.

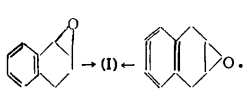
Braun and coworkers [8] obtained β-tetralone, together with α-tetralone, by the oxidation of tetralin with chromyl chloride (Étard reaction); it was shown later [9] that in this reaction both ketones are formed in approximately equal amounts. β-Tetralone is formed in the pyrolysis of trimethyl-(1,2,3,4-tetrahydro-2-hydroxynaphth-1-yl)ammonium iodide [8] and of trimethyl-(1,2,3,4-tetrahydro-2-methoxynaphth-1-yl)ammonium iodide [10] with subsequent hydrolysis of the 3,4-dihydronaphth-2-yl methyl ether:



Crowley and Robinson [11] describe the synthesis of β-tetralone and 6-methoxy-β-tetralone by the Curtius decomposition of the azides of the corresponding 3,4-dihydro-2-naphthoic acids and hydrolysis of the resulting isocyanates:

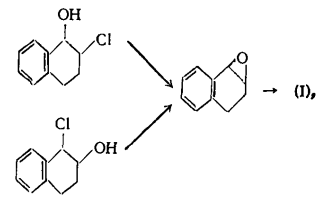


Straus and Rohrbacher [12] obtained β-tetralone in the decomposition of epoxy-3,4- and epoxy-1,4-dihydronaphthalenes and also by dehydrobromination of 1-bromo-1,2,3,4-tetrahydro-2-naphthol:



Tchoubar [13] obtained similar results. Probably the intermediate formation and decomposition of an oxide formed the basis of the production of β-tetralone in the autoxidation of 3,4-dihydronaphthalene by air [14].

The reaction for the preparation of β-tetralone from chlorotetrahydronaphthols also passes through a stage in which epoxynaphthalenes are formed [15]:



and therefore the same ketone is obtained from both isomers.

The method of decomposing epoxydihydronaphthalenes subsequently proved to be extremely useful for synthesising substituted β-tetralone derivatives.

Tchoubar [16] describes the formation of β-tetralone from the cyanohydrin of indan-2-one by hydrogenation and then deamination of the aminoalcohol obtained by the action of nitrous acid.

Compounds of the 2-naphthol series were found to be valuable starting materials for preparing β-tetralone and its derivatives. Thus Robinson and coworkers [17] obtained β-tetralone by the reduction of methyl 2-naphthyl ether with sodium and alcohol followed by hydrolysis of the 3,4-dihydronaphth-2-yl methyl ether formed. Ethyl 2-naphthyl ether behaves similarly [18].

The structure of the intermediate 3,4-dihydronaphth-2-yl methyl ether is confirmed by ozonolysis [19]. β-Tetralone, 7-methoxy-β-tetralone, and 7,8-dimethoxy-β-tetralone [20] are obtained in high yield in the electroreduction of the methyl ethers of the corresponding naphthols.

Birch [21] reduced 2-naphthol to β-tetralone by the action of sodium and alcohol in liquid ammonia. Subsequently the reaction was studied more thoroughly [22] and the side-products were investigated.

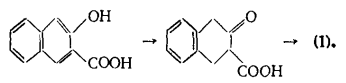
The Robinson–Cornforth and Birch methods are widely used for the synthesis of various substituted β-tetralone derivatives.

2-Naphthol is hydrogenated under severe conditions to β-tetralone [23,24] over palladium deposited on carbon, in the presence of organic bases, and over copper chromite — to 1,2,3,4-tetrahydro-2-naphthol [25], which is dehydrated by ethylene over a catalyst to β-tetralone.

Weil [26,27] obtained β-tetralone by reducing 2-hydroxy-3-naphthoic acid with sodium amalgam, but erroneously ascribed to the product the structure 1,2,3,4-tetrahydronaphthalene-3-carbaldehyde; the same product was obtained by him in reducing various 1-substituted (acetyl, amino-, chloro-, bromo-) 2-hydroxy-3-naphthoic acids.

Weil's erroneous opinion about the structure of his product was corrected by Przhiyalgovskaya and coworkers [28], who showed that when 2-hydroxy-3-naphthoic acid is reduced by sodium amalgam it gives the 3-carboxylic acid of

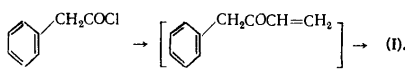
β-tetralone, which is readily decarboxylated into β-tetralone:



(I).

2-Hydroxy-1-naphthoic acid is reduced similarly, but in somewhat less yield[29].

Phenylacetyl chloride gives β-tetralone on reacting with ethylene in the presence of aluminium chloride[30]:



(I).

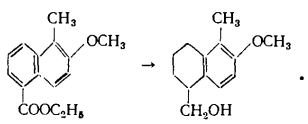
7-Methoxy-β-tetralone is obtained similarly. Much earlier this reaction was used for the synthesis of 4,4-dimethyl- and 3,4,4-trimethyl-β-tetralones[31,32] and 1-isopropyl-4,7--dimethyl-β-tetralone[33].

Of the methods for making β-tetralone which have been described, the following are sufficiently universal, that is, suitable for the synthesis of substituted derivatives: reduction of compounds of the 2-naphthol series after Robinson–Cornforth and Birch, amalgam reduction of hydroxynaphthoic acids, and decomposition of epoxydihydronaphthalenes.

Thus, reduction of the corresponding naphthyl ethers has yielded: 5-methoxy-β-tetralone[27,34-36], 6-methoxy-β--tetralone[17], 7-methoxy-β-tetralone[37-40], 5-methoxymethyl-β-tetralone[41], 5-methoxy-1-methyl-β-tetralone[17,42], 5-hydroxy-1-methyl-β-tetralone[34], 5,8-dimethoxy-β--tetralone[43-47], 7,8-dimethoxy-β-tetralone[38,48], 5-acetamido-β-tetralone[42], 1-methyl-β-tetralone[17], 6-methyl-β--tetralone, and 6-vinyl-β-tetralone[49,50], 6-n-hexyl-β--tetralone[51], 6-(1-hydroxyethyl)-β-tetralone[52], 6-vinyl--β-tetralone[52], 5-(1-ethyl-1,3-dihydroxy-2,2-dimethylpropyl)-β-tetralone[52], 2-(2-hydroxy-2-methylpropyl)--1-methyl-3-(5,6,7,8-tetrahydro-6-oxo-2-naphthyl)cyclopentanol[52], 5-acetamido-4-carboxy-β-tetralone[53].

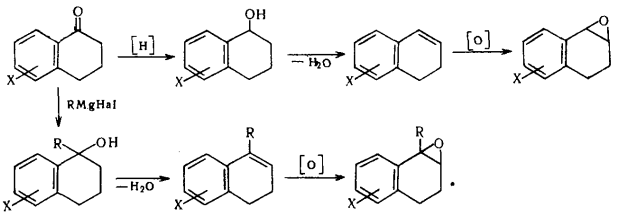
The reaction is usually carried out in an excess of alcohol — sometimes in an inert solvent (toluene)[51] — or in liquid ammonia[19,34,41,42,54].

The reduction of naphthyl ethers does not always proceed smoothly. Robinson and coworkers[17] note that the 1-methyl-β-tetralones are obtained in poor yield, but in a subsequent communication[42] they report a higher yield. The yield was low also for 5-acetamido-β-tetralone[42] owing to the loss of the acetyl residue during the reaction and the tarring of the aminoketone produced. In the reduction of 6-bromo-2-naphthyl methyl ether[52] debromination occurs; sometimes dehydration takes place when there is an alcohol group in a side-chain[52]; with ethyl 6-methoxy--5-methyl-2-naphthoate[52] the nucleus which contains the ethoxycarbonyl group is reduced; simultaneously hydrogenation and esterification of the group occurs and 1,2,3,4-tetrahydro-2-hydroxymethyl-6-methoxy-5-methyl naphthalene is obtained:



6-n-Hexyl-β-tetralone[51] and 6-isopropyl-β-tetralone[54,55] were obtained by reduction by the Birch method. Among the merits of the method are the mild conditions (low temperature, no large excess of sodium); sometimes, however, the yield is worse[51] than by the Robinson–Conforth method.

Decomposition of epoxydihydronaphthalenes provides a rather simple method of obtaining compounds of the β-tetralone series, as epoxy-3,4-dihydronaphthalenes can be synthesised from α-tetralones:



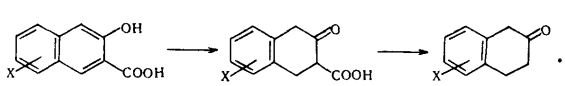
Hence a simple conversion from the readily available α-tetralones to the more difficultly accessible β-tetralones is provided. The following have been synthesised by this method: 6-methoxy-β-tetralone[56-61], 1-methyl-β-tetralone[62-65], 1-ethyl-β-tetralone[65], 1-phenyl-β-tetralone[66,68-71], 1-(2-biphenylyl)-β-tetralone[63,73], 5-methoxy-1-methyl-β--tetralone[63,74,75], 7-methoxy-1,6-dimethyl-β-tetralone[76,77], 7-isopropyl-6-methoxy-1-methyl-β-tetralone[78], 6,7-dimethoxy-1-methyl-β-tetralone[63], 5,8-dihydroxy-1-methyl--β-tetralone and its ethers at the hydroxyl group[79-81], 5,6-dimethoxy-1-methyl-β-tetralone[82], 5-isopropyl-6--methoxy-1-methyl-β-tetralone[83]. This is the best of all the known methods for synthesising 1-alkyl-β-tetralones.

The following oxidants have been proposed for the conversion of 3,4-dihydronaphthalenes into β-tetralone: peracids: perbenzoic[56-59,62,63,68,69,71,72,75-79,83], perphthalic[56,58,72,79], peracetic[60,61,66]; or a solution of hydrogen peroxide in acetic acid in the presence of ammonium molybdate[65,70]; and also inorganic oxidants: osmium tetroxide[79-81], Pb_3O_4 in acetic acid and lead tetra-acetate[63,64,67,73,74,79,82], or potassium permanganate in alkali[62]. Howell and Taylor[63] consider that the best results are given by perbenzoic acid.

After oxidation, ketones are often obtained directly[56-58,62,63,72,75,79], but sometimes an intermediate epoxide is obtained, which on decomposition (for example, by sulphuric acid) gives a diol, which is immediately dehydrated to a ketone[59,63,68,72]. The diols were isolated as diacetates when Pb_3O_4 in acetic acid was used for the oxiation; the diacetates were readily hydrolysed into ketones.

It is noted[65,66,70] that in the oxidation of dehydronaphthalenes by peracetic acid products of the oxidation of the hydrogenated naphthalene nucleus are formed as well as the ketone and diol.

Comparatively recently there was an interesting proposal of a new method for obtaining β-tetralone by reducing 2-hydroxy-3-naphthoic acid by sodium amalgam. It is found that substituted 2-hydroxy-3-naphthoic acids are converted, like the unsubstituted acid, into the corresponding β-tetralones:



6-Bromo-β-tetralone[84], 6-acetamido-β-tetralone[85], and 7-methoxy-β-tetralone[86] were obtained in this way.

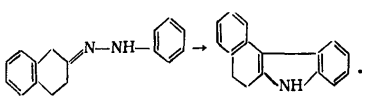
The method of indirect electroreduction differs favourably from the methods described above for preparing β-tetralones, by its mild reaction conditions. The substance to be reduced is treated in neutral or weakly acid medium (pH 6–7) at room or reduced temperature with very dilute sodium amalgam. Thanks to this even in the most complex instances, such as the preparation of halogenotetralones and acylaminotetralones, the reaction proceeds unambiguously and the substituted β-tetralones are obtained in good yields.

Other preparations of certain substituted β-tetralones have been described but have a partial nature and will not be described here. This relates to 1,1-dimethyl-β-tetralone[87,88], 1,3,3-trimethyl- and 1,3,3,7-tetramethyl-β-tetralones[89], 1-chloromethyl-1-methyl-β-tetralone[87], 1-dichloromethyl-1-methyl-β-tetralone[90], 5-bromo-7,8-dimethoxy--1-methoxycarbonyl-β-tetralone[91], 5,8-dimethoxy-β-tetralone[20,47], and 1,1,4,4-tetramethyl-β-tetralone[92].

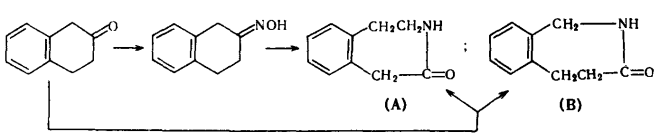
III. CHEMICAL PROPERTIES OF COMPOUNDS OF THE β-TETRALONE SERIES

β-Tetralone forms derivatives at the keto-group; the semicarbazone[8,12], phenylhydrazone[8,12], oxime[12,96], and 2,4-dinitrophenylhydrazone[28] have been described.

Some of these derivatives have been used in organic syntheses. Thus β-tetralonephenylhydrazone[93,94] and 5-, 6-, and 8-quinolylhydrazones[95] are cyclised by the method of Fischer into the corresponding dihydrobenzocarbazoles:



Knunyants and Fabrichnyi[96] carried out a Beckmann rearrangement of the β-tetralone oxime, and obtained the lactam (A):



In addition to this, lactams (A) and (B) were obtained[96] by the action of hydrazoic acid on β-tetralone.

The Beckmann rearrangement of the 1,1-dimethyl-β--tetralone and 1,1,4,4-tetramethyl-β-tetralone have also been studied[97].

β-Tetralone gives a crystalline bisulphite compound[1-3], but one is not formed (probably because of steric hindrance) when there is a basic substituent in position 1 of β-tetralone[17].

β-Tetralone forms an enol acetate when heated with acetic anhydride and sodium acetate[98].

The formation of a cyclic ketal with ethylene glycol has been described for 5-bromo-7,8-dimethoxy-1-methoxycarbonyl-β-tetralone[91].

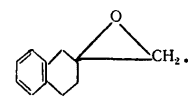
The keto-group in the compounds of the β-tetralone series is reduced after Kishner into a CH_2 group[43,99,100] and also into a hydroxyl group, by aluminium isopropoxide[101,102], lithium tetrahydroaluminate[41,92], and hydrogen over Raney nickel[33].

2,2-Dichloro-1,2,3,4-tetrahydronaphthalene is formed in the reaction of β-tetralone with phosphorus pentachloride.

The ketones of the β-tetralone series react with organomagnesium compounds[8,40,50,51,104,105] and organolithium compounds[106], and undergo a Reformatsky reaction[89,107,108] to form tertiary alcohols.

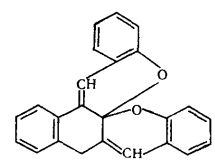
However, the yields in these reactions are usually low because the enols which are readily formed by β-tetralones decompose the organometallic compounds.

Mosettig and Burger[109] carried out the reaction of β-tetralone with diazomethane; ring expansion did not occur but an epoxide of the following structure was formed:

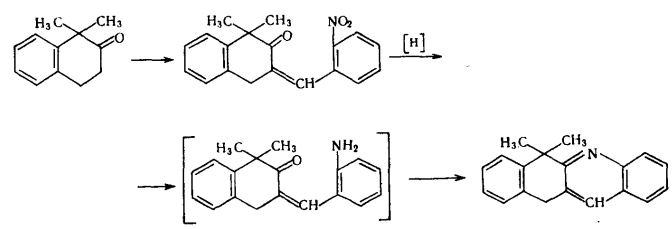


The authors did not isolate the reaction product, but its structure is confirmed by various transformations.

Braun and coworkers[8] condensed β-tetralone with aldehydes in alkali but could not isolate any definite product. Condensation proceeded normally in acid[110]; 1,3-dibenzylidene-β-tetralone and 1,3-disalicylal-β-tetralone (the latter in the form of a ketal) were obtained:



Cromwell and David[111] condensed 1,1-dimethyl-β-tetralone with *o*-nitrobenzaldehyde to synthesise substituted dihydrobenzacridines:

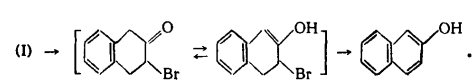


Condensation with aldehydes can be used to characterise substituted β-tetralones[106].

Braun and coworkers[8] studied the bromination of β-tetralone but did not establish the structure of the product. Soffer and coworkers[112] showed that on bromination in ether β-tetralone is dehydrated and forms 2-naphthol with a yield close to quantitative.

In chlorination, β-tetralone gives the stable 3-chloro--β-tetralone[102]; the same compound is obtained[103] by the decomposition of 3-chloro-1,4-dihydronaphthalene.

The formation of 2-naphthol in the bromination of β-tetralone becomes understandable when it is assumed that the first stage of the reaction is the formation of 3-bromo--β-tetralone, which is dehydrobrominated to form 2-naphthol:



The method of converting β-tetralones into 2-naphthols can be applied to a variety of β-tetralones substituted either in the aromatic or in the aliphatic nuclei of the molecule, dehydrogenation by bromine giving the best results [84-86,113].

The methods of studying the structure of compounds of the β-tetralone series have not been developed in the literature. The 2-naphthol derivatives formed in dehydrogenation by bromine have been rather fully described in the literature; therefore the method described above can be recommended for finding the structure of various compounds in the β-tetralone series.

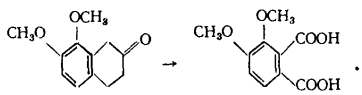
1,1-Dialkyl-substituted β-tetralones — 1,1-dimethyl-β--tetralone [114,115] and 1-(2-dimethylaminoethyl)-1-methyl--β-tetralone [100,116,117] — are brominated in position 3.

Einhorn and Lumsden [4] in oxidising β-tetralone with dilute nitric acid, obtained a dibasic acid to which was ascribed the structure of *o*-phenylenediacetic acid. However, Hückel and Friedrich [118] found that this compound is 2-(2-carboxyphenyl)propionic acid, that is, the bond between the first and second carbon atoms in the hydrogenated ring is broken.

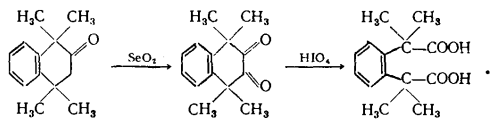
There are analogous results in the oxidation of β-tetralone by peracetic acid [119].

The formation of 2-(2-carboxyphenyl)propionic acid has also been observed in the vacuum distillation of β-tetralone in a stream of air [29].

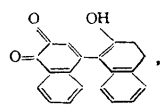
Oxidation under more drastic conditions completely destroys the hydrogenated ring; thus, on oxidation by permanganate in alkali 7,8-dimethoxy-β-tetralone gives the corresponding dimethoxyphthalic acid [38]:



The oxidation of 1,1,4,4-tetramethyl-β-tetralone has been described [120,121]; *o*-di-t-butyl benzene is obtained through *o*-phenylenedi-isobutyric acid:



On treating β-tetralone with alkali in the air it becomes intensely blue [12]. An analogous coloration is also produced in the presence of aliphatic amines [119]. The reaction is characteristic for all the β-tetralones unsubstituted in the first position [11]. The reaction is very sensitive and can be used to detect traces of β-tetralones. In studying this reaction, German investigators [110] showed that β-tetralone is rapidly oxidised in alkali by atmospheric oxygen, with the formation of 4-(3,4-dihydro-2-hydroxynaphth-1-yl)--1,2-naphthaquinone:



to which the blueness of the solution is due.

The Cornforths and Robinson [17] observed that β-tetralone is methylated in position 1 on heating with methyl iodide and sodium isopropoxide in isopropyl alcohol; by this method they obtained 1-methyl-β-tetralone.

The great ease of alkylation of β-tetralone compared with the aliphatic ketones explains its tendency to enolisation in alkali by conjugation of the double bond formed with the aromatic nucleus.

Subsequently similar reactions were studied both for β-tetralone and various substituted β-tetralones. Some think [91] that the process takes place in a single stage and that a mixture of products of 1-mono- and 1,1-di--alkylation is formed, this being difficult to separate. Some compounds, for example, 5-methoxy-β-tetralone [17,34] and 5,8-dimethoxy-β-tetralone [43] are methylated so readily that the monoalkylation product is not obtained at all, or is obtained in only insignificant quantities. The use of potassium t-butoxide [87,99,122] in this reaction improves the yield of monoalkylation products.

It is much more convenient to carry out the reaction not in alcohol, but in an inert solvent using as the base metallic sodium, potassium, sodium hydride, or sodium amide. By varying the molar ratio of the reagents it proved possible to introduce sharply one or two alkyl substituents, including also those instances when alkylation in alcohol was unsuccessful.

It is also possible to introduce two different radicals into position 1 of the β-tetralones, by performing the alkylation successively with different alkyl halides [106,116,123].

The following is the order of activity of the condensing media:

$$NaH \simeq NaNH_2 > K > Na \simeq t\text{-}C_4H_9OK > (CH_3)_2CHONa > CH_3ONa.$$

Carrying out the reaction in an atmosphere of inert gas is recommended, as β-tetralone in alkali is oxidised by air.

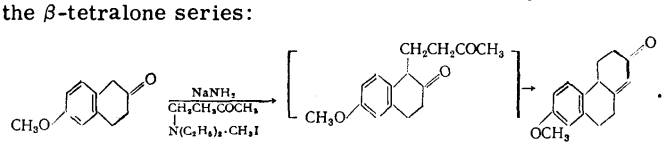
Examples of the alkylation of compounds of the β-tetralone series which have been described are given in the Table.

In recent years the Stork reaction has been used with success for the alkylation of β-tetralones — alkylation of the enamines of the β-tetralones [37,54,55,67,117,132-134]. 1-Alkyl-β-tetralones are obtained by this method in good yields and free from 1,1-dialkyl-β-tetralones as impurities.

Biquard [135-137] described the ultraviolet and Raman spectra of β-tetralone. The infrared spectra of some substituted β-tetralones have also been described. The relation between the structure and the infrared spectra of β-tetralones substituted in the aromatic and aliphatic nuclei of the molecule have also been studied [138].

IV. SYNTHESIS OF NATURAL PRODUCTS AND THEIR ANALOGUES ON THE BASIS OF COMPOUNDS OF THE β-TETRALONE SERIES

Crowley and Robinson [11] suggested a method of constructing phenanthrene systems by starting from compounds of the β-tetralone series:



Methyl vinyl ketone [73,79,139] and ethyl vinyl ketone [73,139] can also be used in this reaction.

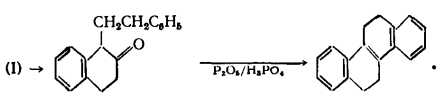
The synthesis opens great possibilities, as the most diverse substituted β-tetralones can be used in it. The

TABLE. Preparation of 1-substituted β-tetralone derivatives.

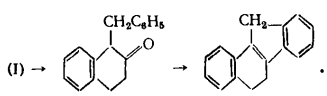
Initial ketone	Substituent introduced	Degree of substitution	Reference
β-Tetralone	methyl	mono-	17,67,123
	methyl	di-	48,87,115
	allyl	mono-	101,124
	benzyl	mono-	125
	m-methoxybenzyl	mono-	125
	phenethyl	mono-	59,125
	2-dimethylaminoethyl	mono-	126
	2-diethylaminoethyl	mono-	125,127
	2-piperidinoethyl	mono-	127
	3-piperidinopropyl	mono-	127
	2-methoxyethyl	mono-	126
	2-benzyloxy	mono-	104
	1-methoxycarbonylethyl	mono-	128
	2-ethoxycarbonylethyl	mono-	129
	3-methoxycarbonylpropyl	mono-	129
	3-cyanopropyl	mono-	129
	methoxycarbonylmethyl	di-	48,99
	cyanomethyl	di-	48
	2-methoxycarbonylethyl	di-	48
	2-ethoxycarbonylethyl	di-	99,129
	2-cyanoethyl	di-	99
	3-methoxycarbonylpropyl	di-	129
	3-cyanopropyl	di-	129
1-Methyl-β-tetralone	2-dimethylaminoethyl		100
	2-diethylaminoethyl		116
	2-ethoxycarbonylethyl		123
3-Methyl-β-tetralone	methyl	mono-	113
5-Methoxy-β-tetralone	methyl	mono-	34,35
	methyl	di-	17
	phenethyl	mono-	122,130
	3-methoxyphenethyl	mono-	122,130
6-Methoxy-β-tetralone	3-methoxybenzyl	mono-	125
	3-methoxyphenethyl	mono-	59,125
	2-ethoxycarbonylethyl	mono-	129
	3-methoxycarbonylpropyl	mono-	
	3-cyanopropyl	mono-	
7-Methoxy-β-tetralone	methyl	mono-	37
	ethyl	mono-	117
5,8-Dimethoxy-β-tetralone	methyl	mono-	43,131
	methyl	di-	43,131
7,8-Dimethoxy-β-tetralone	methyl	mono-	106
	ethyl	mono-	
	2-ethyl-1-methyl	di-	
7,8-Dimethoxy-1-methyl-β-tetralone	ethyl		106
7-Methoxy-1,6-dimethyl-β-tetralone	4-oxo-hexyl		76,77

phenanthrene group is present in extremely important natural products — steroids, the alkaloids of the morphine series, terpenes, resin acids. It is understandable, therefore, that the synthesis proposed by Robinson immediately aroused lively interest and work in this direction is continuing even now [34-37,43,54,55,63,67,74-78,80-82,123,126,134,139-142]. As a result of these investigations several complex natural compounds and their synthetic analogues have been obtained.

Salzer [59,143] used β-tetralone and 6-methoxy-β-tetralone for the synthesis of the tetracyclic chrysene system:

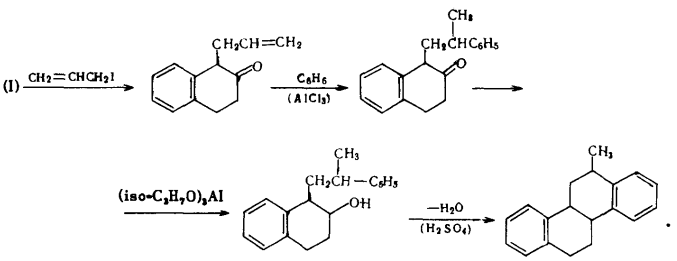


Pentacyclic systems can be obtained similarly by using naphthylethyl bromide for the alkylation [144]. Benzofluorenes have also been synthesised like this [143,145]:

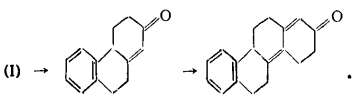


5-Methoxy-β-tetralone was alkylated with 2-phenylethyl bromide and 2-(*o*-methoxyphenyl)ethyl bromide and the compounds obtained were cyclised to chrysenes [122,130].

Indian investigators [101,124] propose an original method for synthesising chrysenes [101,124]:

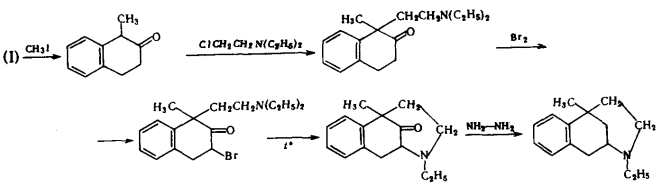


A method for obtaining tetracyclic compounds by successive repetition of the Robinson phenanthrene synthesis has been described [139,146,147]:



Among the compounds of the chrysene series which have been synthesised there are steroid analogues with a six-membered *D* ring and also carcinogenic substances.

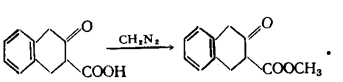
The compounds of the β-tetralone series have been used for building heterocyclic structures similar to morphine. A bicyclic analogue of morphine (benzomorphan) was thus obtained [116]:



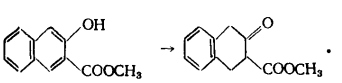
and then the tricyclic analogue [126]. May and coworkers have studied the chemistry of the benzomorphanes [100,105,117,148].

As is evident from what has been said above, various syntheses are based on the high reactivity of the hydrogen atoms in position 1 of the β-tetralone molecule. The first stage of a synthesis is usually the introduction of a substituent into this position of the molecule and then further substitutions are carried out.

The methyl ester of β-tetralone-3-carboxylic acid has recently become available, having been obtained for the first time by the authors of the present review [149]:



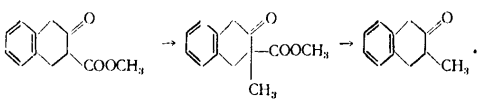
A convenient preparative method for obtaining this ester is the reduction of methyl 3-hydroxy-2-naphthoate with sodium and alcohol in liquid ammonia [150]:



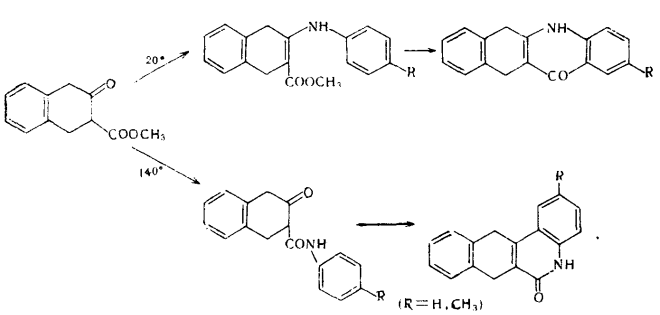
The methyl esters of the 6-bromo-, 6-acetamido-, and 7-methoxy-β-tetralone-3-carboxylic acids have been obtained from the substituted β-tetralone-3-carboxylic acids [84-86].

Pelletier and Parthasarathy [151] obtained 5-methoxy--β-tetralone-3-carboxylic acid and its methyl ester by treating 5-methoxy-β-tetralone with methylmagnesium carbonate. All these compounds contain a labile hydrogen atom in position 3 and therefore are of independent synthetic interest.

By the example of the simplest of these, methyl β-tetralone-3-carboxylate, Przhivalgovskaya and coworkers carried out a series of transformations. This ester was unambiguously methylated in position 3, which makes possible the simple preparation, after ketonic cleavage, of previously inaccessible 3-substituted β-tetralones [113]:



The condensation of methyl β-tetralone-3-carboxylate with aromatic amines [152] takes place at the carbonyl or the ester group according to the conditions. Further conversion of the condensation products allows them to be changed into complex heterocyclic compounds of the benzacridine and benzophenanthridine series containing a dihydronaphthalene nucleus.



The use of the esters of β-tetralone-3-carboxylic acid and the substituted acids for other synthetic purposes is very promising.

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CHEMICAL METHODS OF SYNTHESIS OF POLYNUCLEOTIDES

S. M. Zhenodarova and M. I. Khabarova

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I. INTRODUCTION

The problems of the synthesis of polynucleotides are now attracting attention from scientists. Enzymes have been used to obtain deoxyribopolynucleotides [1] and ribopolynucleotides [2-5] of high molecular weight (from 30 000 to 2 000 000) and a random distribution of purine and pyrimidine bases along the polynucleotide chain, which have played an exceptionally important role in investigations which have been undertaken as the start of the study of the amino-acid code [6,7]. For several investigations there is a need for polynucleotides of definite composition and comparatively low molecular weight [8,9]. In studying the influence of the chain length of polyuridylic acid on the inclusion of phenylalanine in a cell-free yeast system it was found that the polyuridylic acid is active from the nonanucleotide onwards [10]. A sharp increase in the inclusion of phenylalanine was noted on going from U_8† to U_9 from U_{11} to U_{12} and from U_{14} to U_{16} (up to U_{22} studied), but for definite conclusions it was necessary to check the results on pure specimens of the polynucleotides.

† The nomenclature, abbreviations, and representation in diagrams corresponds to that generally accepted [11,12].

Preliminary experiments with hexauridylic acid having a terminal 3′-phosphate group showed that in a mixture with a high-polymer polyuridylic acid the hexanucleotide inhibits its activity by ~30% in relation to the synthesis of polyphenylalanine [13]. When hexauridylic acid is treated with dicyclohexylcarbodiimide (DCC) under conditions leading to the cyclisation of the 3′-monophosphate into the 2′,3′-cyclic phosphate, inhibition is not observed. An analogous effect, but with oligouridylic acids having a terminal 5′-phosphomonoester group was observed by Jones and coworkers [14]. The dependence of the synthesis of peptides of lysine on the length of the polyadenylic acid chain has also been noted [15].

Homopolynucleotides with different terminal groups are frequently used in work to determine the specificity of nucleases [16-18] and as formerly is of interest for determining the sequence of the purine and pyrimidine bases in the nucleic acids and in the investigations of enzymes which synthesise the nucleic acids [19].

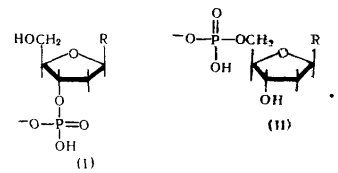
The availability of polynucleotide with a chain of known dimensions, known composition, and with known terminal groups should facilitate the study of systems which synthesise polypeptides, and apparently show the direction of further work on the synthesis of specific ribopolynucleotides of interest in the study of the amino-acid code [20]. The problems connected with obtaining such polynucleotides should also be solved by chemical methods of polynucleotide synthesis.

Chemical methods of synthesising polynucleotides are developing in two directions: (1) the stepwise synthesis of oligonucleotides, and (2) polycondensation. The stepwise synthesis of oligonucleotides recently formed the subject of a special review [21]. The present review will consider methods of synthesising polynucleotides by condensation‡ of mononucleotides or other "monomeric" units.

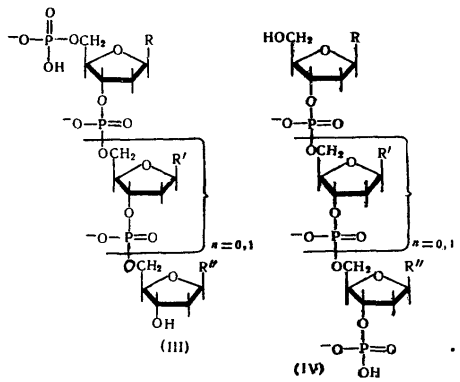
II. METHODS OF POLYMERISATION

1. Types of "Monomers"

It must be specially emphasised that in developing methods of synthesis of polynucleotides it must be taken into account that the polymeric chain should be formed by molecules of sugar (deoxy-D-ribose or D-ribose) joined by residues of phosphoric acid through the OH-group at the $C_{(3')}$ atom of one carbohydrate molecule and the OH group at the $C_{(5)}$ atom of another. In accordance with this requirement, the "monomers" for obtaining the polynucleotides can be derivatives of nucleotides of the following types: (a) for the deoxyribopolynucleotides series:

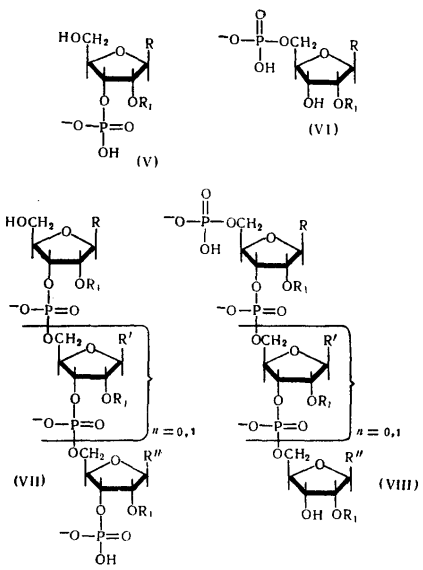


‡ Usually in the literature devoted to the problems of obtaining polynucleotides this method is inaccurately termed polymerisation; we will keep to this name subsequently as it is the most widely employed.



(III) (IV)

(b) for the ribopolynucleotides series:



(V) (VI) (VII) (VIII)

where R, R′, and R″ are purine or pyrimidine bases with protected amino-groups for adenine, guanine, and cytosine, and R_1 is acyl or alkyl. Of the types of monomer listed, the following have been used for the synthesis of polynucleotides:

(I) R = thymine [22-24].
(II) (a) R = thymine [25,26]; (b) R = *N*-benzoyladenine [27]; (c) R = *N*-anisylcytosine [28]; (d) R = *N*-acetylguanine [29].
(III) n = 0; (a) R = *N*-anisylcytosine, R″ = *N*-acetylguanine [12]; (b) R = thymine, R″ = *N*-benzoyladenine [30]; (c) R = *N*-anisylcytosine, R″ = thymine [31].
(V) (a) R = *N*-benzoyladenine, R_1 = acetyl [32]; (b) R = = uracil, R_1 = acetyl [13,33].

Khorana and coworkers [30] proposed to obtain a monomer of type (IV), but there has not yet been any work in this direction. Monomers of types (VI) and (VIII) cannot be obtained at present (there are still no methods which allow the hydroxyl group at the $C_{(2')}$ atom to be selectively protected when there is a free hydroxyl group at $C_{(3')}$). Monomers of type (VII) can be obtained but have not yet been described. There is only a brief reference [34] to the use of the following trinucleotides as a monomer: (1) (VII) with n = 1, R = adenine, R′ = guanine, R″ = cytosine, R_1 = = H; (2) (VII) with n = 1, R = adenine, R′ = guanine, R″ = = uracil, R_1 = H.

In addition to those listed, the starting materials for polymerisation have included nucleoside-2′,3′ cyclicphosphates [35], but monomers of this type form both $C_{(3')}$–$C_{(5')}$ and $C_{(2')}$–$C_{(5')}$ internucleotide bonds in polymerisation, therefore they are not of great interest (see below for details).

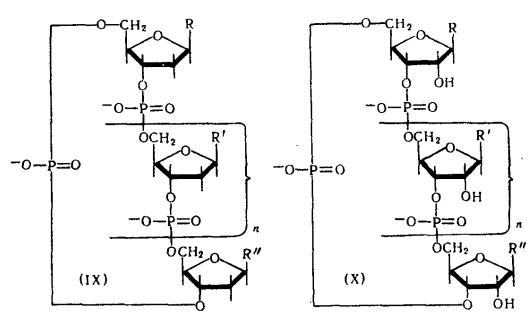
2. Conditions for the Polymerisation, Isolation, and Identification of Polynucleotides

The polymerisation of appropriate monomers is usually brought about by use of such activating agents as DCC [dicyclohexylcarbodi-imide (Ed. of Translation)][25], *p*-toluenesulphonyl chloride [25], diphenyl phosphorochloridate [36], tetraethyl pyrophosphate [34], enol phosphates [37], polyphosphates [38], etc. The analysis of mixtures obtained in polymerisation in the presence of the above substances shows that the most suitable activating agent is DCC, since with all the others the mixture is more complex. An attempt to obtain a more homogeneous reaction mixture by the carbodi-imide method, using di-isopropylcarbodi--imide, was not successful, since in the presence of the latter polynucleotides with a rather less degree of polymerisation are obtained [11].

Usually the polymerisation is carried out in anhydrous pyridine solution at room temperature for 4–7 days. The concentration of the monomer in the reaction mixture is 1 M, that of DCC up to 2.5 M. The mixture of polymers is usually subjected to dialysis and separated by chromatography on DEAE or ECTEOLA-cellulose and paper chromatography. The chain length is determined by enzymic splitting of the corresponding polynucleotide to the nucleoside-3′ phosphate and nucleoside with subsequent determination of their concentrations by the methods of paper chromatography and spectrophotometry, and also by direct comparison with specimens obtained by partial enzymic splitting of the corresponding polynucleotide of high-molecular weight [13].

It has been found that the reaction mixture is quite complex: it contains linear polynucleotides, cyclic polynucleotides, non-symmetrical pyrophosphates, nucleoside-2′,3′ or nucleoside-3′,5′ cyclic phosphates, 5′-*C*-pyridinium nucleoside-3′ phosphates, and also several unidentified side-products.

The linear polynucleotides — (III), n = 0–10; (VII), n = = 0–8 — contain a different number of nucleotide residues, depending on the initial monomer, but not more than 12 (linear polynucleotides of higher molecular weight are present in the reaction mixture but they were not identified):



(IX) (X)

where R, R′, and R″ are purine or pyrimidine bases.

The cyclic polynucleotides (IX) and (X) are formed in large amounts (up to 16–18%) (with increase in the chain length their proportion decreases) and for pyrimidine monomers cyclic dinucleotides — (IX), (X), $n = 0$ — are formed predominantly[25], whereas for purine monomers, the formation of cyclic trinucleotides — (IX), (X), $n = 1$ — is characteristic[27,29]. Mixed monomers — for example, (III)(b) — form cyclodinucleotides[12].

To suppress the formation of cyclic forms, attempts were made to find new conditions for polymerisation[26]. The derivative of another nucleotide which would be the start of polymeric chains incapable of cyclisation was added to the mixture being polymerised, more concentrated solutions were used, monomers were taken admixed with a derivative of the same nucleotide but having only one phosphate group free — for example; (1) pT + pT-OAc§ (3 : 1)[26]; (2) (d)-pC^{An} + (d)-C^{An}-OAc (3 : 1)[28]; etc. The use of such a mixture for polymerisation is especially desirable in the ribonucleotide series, since the nucleoside-3′ phosphates — monomers of type (V) — have a greater tendency to form intramolecular 3′,5′-cyclicphosphates[39], than the nucleoside-5′ phosphates which can be used as monomers in the polymerisation of deoxyribonucleotides. Thus the addition of 2′,5′-*O*-diacetyluridine-3′ phosphate to 2′-*O*-acetyluridine-3′ phosphate should suppress side-reactions owing to the acceleration of the formation of oligonucleotide chains having 5′-*O*-acetyl terminal groups[13]. However, these measures have not yet led to a significant change in the results (Table 1).

For the cleavage of pyrophosphates, which are also formed during the polymerisation, the reaction mixture is first treated with aqueous pyridine[13] and then with an excess of acetic anhydride in dry pyridine[40].

In extending the number of monomers it was shown that the standard conditions under which polymerisation is carried out are not always acceptable: in some instances the starting materials are insoluble in pyridine, in others the pyridinium salts formed during dissolution are precipitated. To avoid these difficulties, the medium used was a mixture of pyridine and formamide with Dowex-50 in the pyridinium form[29], a mixture of dimethylformamide and pyridine with Dowex-50 in the pyridinium form[12], or the monomer was changed into another, soluble form (for example, TppT was used instead of Tp)[22].

TABLE 1.

Polynucleotides*	Yield of polynucleotides**, %						
	N = T			N=(d)-A	N=(d)-C	N = A	N = U
	pT	polymerisation of Tp: DCC	polymerisation of Tp: trichloroacetonitrile				
Linear:							
Np		0.1	6.3			26.0	8.3
NpNp	5.83	0.3	4.2	18.31	10.8	20.3	8 3
NpNpNp	9.24	3.5		14.20	15.0	12.0	5.5
NpNpNpNp	8.97	3.4	5.7	12.0	11.35	7.0	4.7
NpNpNpNpNp	7.8	4.0		9.0	8.20	4.2	2.3
$Np(Np)_4Np$	6.70			4.95	5.33		1.1
$Np(Np)_5Np$	5.20			3.09	3.14		1.0
$Np(Np)_6Np$	4.12			1.5	1.84		0.76
$Np(Np)_7Np$	3.19						0.08
$Np(Np)_8Np$	2.57						0.06
$Np(Np)_9Np$	2.07						
$Np(Np)_{10}Np$	1.52						
Higher***	4.71				3.65	3.8	
Cyclic:							
NpNp	10.0	16.5	9.5		32****	3.0	6.7
NpNpNp	3.45	4.0		8.29	2.44	7.0	5.0
NpNpNpNp	1.42	3.1			1.05		
NpNpNpNpNp and unidentified	1.58	3.3					

* N = nucleoside residue.

** The yields are given on the basis of the spectrophotometric results.

*** Unidentified.

**** Yield of cyclodinucleotide + (d)–pC.

§ See the first note on p. 531.

Linear polynucleotides with a small degree of polymerisation (for example, up to hexa-) are isolated, as already noted, by use of ion-exchange chromatography on DEAE-cellulose in the carbonate or hydrogen carbonate form at pH 8–9, by eluting the corresponding fractions with triethylammonium hydrogen carbonate. Polynucleotides of higher molecular wieghts are purified by repeatedly chromatographing appropriate fractions on DEAE-cellulose in the chloride form and using linear gradient elution with solutions of lithium chloride or lithium acetate. The homogeneity of the polynucleotides obtained is confirmed by enzymic treatment and also by chromatography and electrophoresis on paper.

III. HOMOPOLYNUCLEOTIDES

1. Deoxyribopolynucleotides.

Polymers have now been obtained of all four fundamental deoxyribonucleotides. The greatest number of work relates to the production of thymidine polynucleotides. (I), (II)(a) and also TppT have been used as monomers[22]. The reagents which activate the monomers are DCC, trichloroacetonitrile[24], and diethyl 1-ethoxy-2-ethoxy-carbonylvinyl phosphate[23]. The best results were given by polymerisation of (II)(a) mixed with pT-OAc (3 : 1) in anhydrous pyridine in the presence of DCC (in Table 1).

The polymerisation of (II)(b) mixed with (d)-$pA^{Bz}OBz$ (3 : 1) and (II)(c) mixed with (d)-$pC^{Ac}OAc$ (3 : 1) under standard conditions (anhydrous pyridine, DCC, room temperature), with subsequent removal of the protective groups led to a mixture of polymers, of which the constituent with the highest molecular weight had a degree of polymerisation of 8 (higher members were not identified) (see Table 1). The use of this method for obtaining deoxyguanosine polynucleotides met with several difficulties[29]. The monomer (II)(d) was almost insoluble in dry pyridine. Some other protected derivatives of guanosine-5′ phosphate containing more lipophilic groups were therefore obtained: *N*-benzoyl-, *N*-naphthyl, and *N*-di-*p*-methoxytrityl-deoxyguanosine-5′ phosphate. Of these, the last compound is sufficiently soluble in anhydrous pyridine. However, its polymerisation under standard conditions did not gave satisfactory results: 55% of the original monomer, 8% of a dinucleotide, and only 12% of higher oligonucleotides were obtained. Other studies also showed that the size of the protective groups affects the formation of the internucleotide bond[31,41], therefore the derivatives obtained could not be used as monomers. An attempt was made to use for polymerisation salts of *N*-acetylguanosine-5′ phosphate and stronger bases (tri-n-decylamine), which are more soluble in pyridine than the pyridinium derivatives. As the use of DCC as a polymerising agent does not permit such strong bases as trialkylamines to be used[11,42], the salt mentioned was polymerised in the presence of *p*-toluenesulphonyl chloride.

However, the polymerisation mixture was very complex and many of its components could not be identified. The most successful was an attempt to polymerise (II)(d) mixed with dimethylformamide and pyridine by adding the pyridinium form of Dowex-50 to create the proton concentration needed for carrying out the reaction in the presence of DCC[11]. Nevertheless, deoxyguanosine polynucleotides could not be obtained pure and identified by the usual means, since on treating the polymerisation products with concentrated ammonia to remove the *N*-acetyl groups, polymers were obtained which form, according to the results of enzymic studies, high-molecular-weight aggregates with an ordered secondary structure[29,43]. Therefore subsequently the polymerisation mixture (without removal of the protective groups) was separated on a column of DEAE-cellulose in the hydrogen carbonate form under conditions which excluded the detachment of *N*-acetyl groups. Table 2 gives the results.

2. Ribopolynucleotides

The preparation of ribopolynucleotides is a more complex task because the corresponding monomers are less accessible and the reaction mixture contains more components.

Michelson[44] proposed to obtain ribonucleotides by using ribonucleoside-2′,3′ cyclic phosphates as the monomers. Preliminary work with glycerol-2(or 1) phosphate showed that on treatment of the monomer with diphenyl phosphorochloridate or tetraphenyl pyrophosphate[45], a polyglycerophosphoric acid is readily obtained through the intermediate stage of P^1-glycerol-2(1)-P^2-diphenyl pyrophosphate, which is rapidly converted into glycerol-1,2 cyclic phosphate. Similar treatment of adenosine-2′(3′) phosphate with diphenyl phosphorochloridate gives initially adenosine-2′,3′ cyclic phosphate[46], subsequent polymerisation of which leads to a polyadenylic acid with a chain length varying from that of a dinucleotide to polynucleotides containing up to 15 monomeric units.

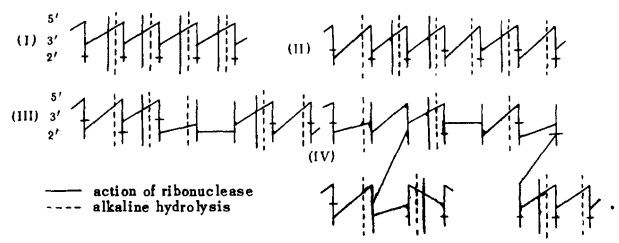
The method is easily extended to the synthesis of polymers of guanosine-2′(3′) phosphate, uridine-2′(3′) phosphate[47], pseudouridine-2′(3′) phosphate[36]. A similar polymerisation of cytidine-2′(3′) phosphate led to a polymer stable against treatment with alkalis and diesterases, and probably containing phosphoramide bonds between the 2′(3′)-phosphate groups and the 6-amino-group of the cytosine. Selective acetylation of the amino-group in cytidine-2′,3′ cyclic phosphate and treatment of the product with diphenyl phosphorochloridate followed by removal of the acetyl groups allowed polycytidylic acids with chains of various lengths to be obtained[36].

In addition polymers have been obtained from analogues of nucleotides, including *N*-methyluridylic, 5-bromouridylic, and 5-iodouridylic acids[48]. The mean chain lengths of the polymers thus obtained amounted to 10–12 nucleotide residues. Study of the properties of these polymers showed that they contain ~50% $C_{(2')}$–$C_{(5')}$ internucleotide bonds.

TABLE 2.

Polynecleotide	Yield, %
N-Acetylguanosine-dinucleotide	15.4
N-Acetylguanosine-trinucleotide	9.4
N-Acetylguanosine-tetranucleotide	5.2
N-Acetylguanosine-pentanucleotide	4.9
Higher	9.78
Cyclotrinucleotide	26.8

Schramm and coworkers[38] reported the preparation of polyadenylic, polycytidylic, polyguanylic, polyuridylic, and polythymidylic acids of high molecular weight (15 000–50 000). To avoid intramolecular cyclisation these authors recommend the use of reaction mixtures as concentrated as possible, by mixing the nucleotides to be polymerised directly with a viscous ester of a polyphosphoric acid. However, the work does not contain a direct proof that the polynucleotides formed contain only $C_{(3')}$–$C_{(5')}$ bonds. At the same time, Kochetkov and coworkers[49] showed that the condensation of a nucleoside-2′(3′) phosphate under the conditions specified can lead theoretically to the formation of compounds of the following types:



Polymers of type (I) should give only mononucleotides on treatment with ribonuclease, polymers of type (II), di- and oligo-nucleotides. Alkaline hydrolysis leads predominantly to mononucleotides with (II) and predominantly to mononucleotides with (III), only with (IV) do both enzymic and alkaline hydrolyses lead to a complex mixture consisting chiefly of oligonucleotides. The results of treating polynucleotides obtained by Schramm's method with ribonuclease and 2*N* KOH suggest that bonds of the non-native type predominate in these polynucleotides.

Khorana and coworkers obtained adenine[32] and uridine[13,33] polynucleotides by taking (V)(a) and (V)(b) as monomers. They treated a mixture of (V)(a) and *N*, 2′, 5′-triacetyladenosine-3′ phosphate (3 : 1) with DCC in dry pyridine by the standard method for 6 days and after the usual treatment (cleavage of the pyrophosphate bonds and removal of the protective groups), the product was separated on DEAE-cellulose (see Table 1). A mixture of (V)(b) and 2′,5′, *O*-diacetyluridine-3′ phosphate was polymerised in a similar way, and after repeated chromatography on DEAE-cellulose polynucleotides up to decauridylic acid inclusive were obtained in an individual state (see Table 1). However, many side-products remained to be identified. They probably contain chiefly two series of compounds: homologous oligonucleotides with 2′3′-cyclic phosphate terminal groups and with 3′-phosphate or 2′,3′-cyclic phosphate groups on one end of the chain and *C*-5′-pyridine group on the other. The presence of a large number of side-products in the polymeric mixture emphasises the additional difficulty of work with ribonucleotides.

IV. HOMOPOLYNUCLEOTIDES WITH DIFFERENT TERMINAL NUCLEOTIDES

Khorana and coworkers[26] have proposed a general method for obtaining homopolynucleotides having another nucleotide

TABLE 3.

Polynucleotides	Yield, %		
	chromatography on DEAE-cellulose	repeated chromatography	
		homo-	mixed
pTpT + (d)-pTpC	13	35	65
pTpTpT + (d)-pTpTpC	15.3	46	54
pTpTpTpT + (d)-pTpTpTpC	9.8	42	58
$pT(pT)_3pT$ + (d)-$pT(pT)_3pC$	8.25	41	59
$pT(pT)_4pT$ + (d)-$pT(pT)_4pC$	5.05	41	59
$pT(pT)_5pT$ + (d)-$pT(pT)_5pC$	3.52	41	59
$pT(pT)_6pT$ + (d)-$pT(pT)_6pC$	2.14	41	59
$pT(pT)_7pT$ + (d)-$pT(pT)_7pC$	1.38	37	63

TABLE 4.

Polynucleotides	Yield, %	Polynucleotides	Yield, %
(d)-TpC	28.0	(d)-pCpCpCpC	4.6
(d)-pTpCpC + cyclo-(d)-pCpC	14.0	(d)-TpCpCpCpCpC	3.3
(d)-pCpC	6.1	(d)-pCpCpCpCpC	4.0
(d)-TpCpCpC	8.7	$(d)\text{-Tp(Cp)}_3\text{C}$	2.3
(d)-pCpCpC + cyclo-(d)-pCpCpC + unidentified	9.7	$(d)\text{-pC(pC)}_4\text{pC}$	2.2
(d)-TpCpCpCpC	7.5	Higher	0.9

at the 3′ end of the chain. The method consists of the addition to a monomer (nucleoside-5′ phosphate) of a completely substituted derivative of another nucleotide. In particular, a mixture of thymidine-5′ phosphate and *NO*-3′-diacetyldeoxycytidine-5′ phosphate was subjected to polymerisation under standard conditions. Table 3 gives the results.

In the same laboratory[12] it was proposed to obtain homopolynucleotides with a distinctive terminal nucleotide by treating the mixture after polymerisation of the nucleoside-5′ phosphate with the appropriate protected nucleoside having a free 3′-OH group, in the presence of a condensing agent. Thus a mixture of *N*-anisyldeoxycytidine polynucleotides immediately after polymerisation was treated with an excess of 5′-*O*-dimethoxytritylthymidine and DCC in anhydrous dimethylformamide. After removing the protective groups and chromatographing the mixture on DEAE-cellulose the results in Table 4 were obtained. Attempts to treat in a similar manner not a mixture of polymers but a purified oligonucleotide showed that best results are obtained in working with a mixture.

V. POLYNUCLEOTIDES WITH A RANDOM DISTRIBUTION OF PURINE AND PYRIMIDINE BASES ALONG THE CHAIN

Polynucleotides consisting of different nucleotide units with a random distribution of purine and pyrimidine bases were obtained by Michelson[47] from various mixtures of nucleoside-2′,3′ cyclic phosphates. However, the copolymers obtained are not of great interest, as they contain, in addition to the $C_{(3')}$–$C_{(5')}$ internucleotide bonds, ~50% $C_{(2')}$–$C_{(5')}$ bonds, and therefore we will not consider them in detail. The longest polynucleotide chain obtained in this way did not exceed 10–12 nucleotide units.

Mixed polynucleotides were also obtained by condensing a mixture of nucleoside-2′(3′) phosphates in the presence of a polyphosphate ester[49]. Table 5 gives information on the reagent proportions, reaction conditions, yields, and compositions of the polymers. As noted above, non-native bonds predominate in these polynucleotides.

VI. POLYNUCLEOTIDES WITH REGULARLY ALTERNATING PURINE AND PYRIMIDINE BASES

At present we know of only three works on the preparation of polynucleotides with regularly alternating bases. In the first, on the polymerisation of dinucleotides[30] the monomer was (III)(b). Interest in studying polynucleotides with such a sequence was stimulated by the knowledge that in some types of crabs there is found a DNA containing predominantly two of these nucleotides in alternating sequence[50-52]. The polymerisation of (III)(b) was carried out in the presence of DCC under standard conditions and after the usual treatment the results shown in Table 6 were obtained.

The study of the ultraviolet absorption (260 nm) as a function of temperature was made in the presence of 1 M NaCl (pH 7) and showed that the polynucleotides obtained have a secondary structure. It was preliminarily found that the dodecanucleotides and the fraction containing higher nucleotides act as seeds for the catalysable DNA-polymerase [DNA nucleotidyltransferase (Ed. of Translation)] synthesis of large T-(d)-A copolymers.

The polymerisation of (III)(a) was effected in a mixture of dimethylformamide, pyridine, and the pyridinium form of Dowex-50 in the presence of DCC. The resulting mixture, after the standard treatment, was separated on DEAE-cellulose in the presence of 7 M urea[53]. It should be noted that in both instances a large amount of a cyclodinucleotide is formed and the degree of polymerisation is not high (Table 7).

Finally, Schramm and coworkers recently published a brief communication[34] on the polymerisation of ApGpCp and AdGpUp in ethyl tetrametaphosphate and trisdimethylaminophosphate. The polymers were separated on Sephadex G-75. Information was not given about the composition of the mixture, degree of polymerisation, etc.

In conclusion, it must once again be emphasised that the methods of chemical synthesis of polynucleotides are now at present quite imperfect and require improvement and further development. In particular, one of the principal

TABLE 5.

Reagents				Reaction conditions		Yield of polymer, %	Composition of bases (A/C or A/U)
AMF, mM	UMF, mM	CMF, mM	PPE*, g	°C	h		
—	2.5	—	24	70—80	40	20—25	—
0.15	—	0.31	3.5	70—75	60	12.2	1:4.5
0.23	—	0.23	3.5	70—75	60	12.5	1:3.3
0.31	—	0.15	3.5	70—75	60	7.6	1:1.4
0.15	0.31	—	4.0	60	30	8.9	1:1.91
0.23	0.23	—	4.0	60	30	5.8	1:0.95
0.31	0.15	—	4.0	60	30	3.2	1:0.58

* PPE = polyphosphate ester.

TABLE 6.

Polynucleotides	Yield, %
Cyclo-(d)-pTpA	36.3
(d)-pTpA	22.6
(d)-pTpApTpA	10.7
(d)-pTpApTpApTpA	5.0
(d)-pTpApTpApTpApTpA	2.0
Higher (~50% decanucleotide)	1.1

TABLE 7.

Polynucleotides	Yield, %
(d)-pCpG	23.2
Cyclo-(d)-pCpG	16.8
(d)-(pCpG, O, pCpG)	18.0
(d)-pCpGpCpG	8.75
(d)-(pCpG, O, pCpGpCpG)	3.43
(d)-pCpGpCpGpCpG + higher + + pyrophosphates	8.75

deficiences in the method is that despite many attempts, it has so far proved impossible to obtain and isolate polynucleotides containing more than 12 nucleotide residues and the yield of the longest of the identified polynucleotides does not exceed 1–2%. In this connection the main tasks of the chemical synthesis of polynucleotides consists in increasing the degree of polymerisation and yield of polymers and also in the development of methods of separating the high-molecular-weight oligonucleotides. It is quite probable that a more careful study of the kinetics and thermodynamics of the polycondensation reactions, a choice of new condensing agents, and the introduction into the "monomer" of more active groups which participate in the reaction are needed. A new approach to the chemical synthesis of polynucleotides should make available polynucleotides with a known succession of purine and pyrimidine bases in the polynucleotide chain, which is known to be impossible in the enzymic synthesis of polynucleotides. This allows the solution on the molecular level of the problems connected with the structure and functions of the nucleic acids, the mechanism of protein synthesis, etc.

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EXPERIMENT AND THE ELECTRONIC THEORY OF CATALYSIS†

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1. INTRODUCTION

In the present lecture I shall endeavour to discuss the electronic theory of catalysis from the point of view of the experimentalist who wishes to apply its results rather than from the point of view of the theoretician who is contributing to its development. I shall be talking of the experimental material on which the theory is based: that which has given rise to the theory and that which, in turn, stems from the theory.

Some simple relationships exist in general (and in the field of catalysis, in particular) between physical theory and experiment which can be expressed by the trite statement that theory divorced from experiment is effectively meaningless whilst experiments lacking a theory are blind. Experiment is the fertile soil in which theory can grow; theory, like a theatrical spotlight, throws light on experiment.

The electronic theory of catalysis has a twofold aim: on the one hand, to reveal the elementary mechanism of the catalytic act and at the same time to discover the relationship between the chemisorption and the catalytic properties of a surface, and on the other hand to relate those characteristics to the electronic properties of the crystal as a whole. The electronic theory of catalysis does not, in general, conflict with other contemporary theories of catalysis: it differs from them only in its approach to the problem. It is concerned with the elementary (electronic) mechanism of the phenomenon, and it tackles problems in catalysis from just this point of view.

The electronic theory of catalysis proved to be the gate through which contemporary solid state theory and the theory of the chemical bond, together with their associated quantum mechanics and quantum statistics, were able to enter the field of catalysis. The history of science has no comparable examples to offer of an invasion by physics of the territory of chemistry. Consider, for instance, the theory of the chemical bond, which even 50 years ago consisted of nothing more than dashes denoting valencies. Quantum mechanics has given those dashes a physical content, thus uncovering the physical nature of chemical forces.

We can distinguish two aspects of the interplay between the electronic theory of catalysis and experiments, which the present article aims to discuss.

Firstly, the theory provides an explanation of known experimental facts. These can be *old* facts, fitting more or less well into old theories, on which the electronic theory throws new light. Or they can be *new* facts, transcending the scope of the older theories, and deriving some theoretical interpretation, for the first time, from the electronic theory.

Secondly, the electronic theory leads to a number of experimental predictions. Like any other theory, it contains explicit or implicit rules and relationships which can be (and should be) identified and tested experimentally.

It is useful and interesting to gather together and analyse the basic experimental material which is satisfactorily interpreted by means of the electronic theory and which can therefore be entered on the credit side.

At the same time, it is particularly interesting to collect and analyse all the corollaries of the electronic theory still awaiting experimental confirmation. Such is the aim of the present paper.

This paper is divided into three sections of unequal length and importance: (1) first of all we shall deal (rather briefly) with some well known experimental facts on which the electronic theory has thrown new light; (2) we shall then list (again, rather briefly) some predictions of the electronic theory which have already been confirmed; (3) lastly, and this will form the major part of the paper, we shall attempt to summarise those theoretical predictions still awaiting experimental confirmation.

2. SOME OLD FACTS IN A NEW LIGHT

a. "Induced" Non-Uniformity

When discussing well-established experimental facts to which the electronic theory has given new meaning one should mention first of all the reluctance of real surfaces to show Langmuir adsorption behaviour.

Classical theory copes with this fact by introducing the concepts of surface non-uniformity or interaction between adsorbate particles. The electronic theory introduces yet a third alternative: a special kind of "interaction, transmitted through the electron gas, which enables each chemisorbed particle to experience the presence of all the others despite the absence of direct force interactions[1,2]. This effect arises because the properties and the nature of the bond between each individual particle and the surface are determined by the state of the whole system of adsorbent + adsorbate. We are also dealing with a special kind of "non-uniformity", because at any given time particles of a single kind form different types of bond with the surface. This is the effect to which Boudart recently applied, rather unsuccessfully, the term "induced non-uniformity".[3]

Allowing for this special kind of "interaction" or of "non-uniformity" — the two concepts are equivalent in this context — brings the Fermi level[4] into the expression for the differential heat of adsorption q. Thus, it follows from the electronic theory that[1]

$$q = q^0 - kT \ln (1 - \eta), \tag{1}$$

where q^0 is the binding energy between a chemisorbed particle in its electrically neutral state and the lattice of the adsorbent, and η is the proportion of the charged form of chemisorption on the surface. The quantity η is of the form

$$\eta = \frac{1}{1 + \exp [\pm (\epsilon_s - v)/kT]}, \tag{2}$$

so that, substituting (2) into (1), we arrive at the following expression for q:

$$q = q^0 + kT \ln \{1 + \exp [\mp (\epsilon_s - v)/kT]\}. \tag{3}$$

The significance of the symbols adopted here is clear from Fig. 1, showing the energy diagram for a semiconductor, on which FF denotes the Fermi level and A is the localised surface level associated with an adsorbed particle. In formulae (2) and (3) we must choose the upper or the lower sign according to whether the adsorbed particle is an acceptor or a donor. If $\eta = 0$, that is, if all the particles are in the same (electrically neutral) state, Eqn. (1) gives $q = q^0$ (the classical result).

The Fermi level ϵ_s, as well as the heat of adsorption q, enters into the isotherm equation

$$\theta = \frac{1}{1 + (b/p) \exp (-q/kT)}, \tag{4}$$

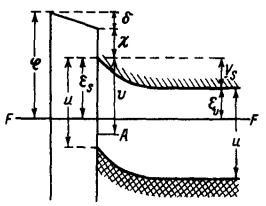

Fig. 1.

where q has the form of (3). Of course, the position of the Fermi level at the crystal surface, ϵ_s, is itself a function of the degree of coverage of the surface, θ:

$$\epsilon_s = \epsilon_s(\theta). \tag{5}$$

Thus, Eqn. (4) is still not an isotherm equation, because it does not explicitly contain the variation of θ with p. By solving Eqn. (4) for θ we obtain various non-Langmuir isotherms (corresponding to different approximations) which agree with experimental observations. This was done by Kogan and Sandomirskii[5] as long ago as in 1959.

In this way, the electronic theory leads to non-Langmuir isotherms for surfaces which are uniform (in the classical sense) and in the absence of interactions between adsorbed particles (again, in the classical sense).

b. Physical Nature of the "Distribution Function" in the Theory of Non-Uniform Surfaces

"Induced non-uniformity", a concept typical of the electronic theory, does not, of course, prelude surface non-uniformity of the usual type. The phenomenological theory of adsorption at a non-uniform surface developed by Roginskii's school[6] can be fitted, in its entirety, into the electronic theory. Furthermore, some of the concepts acquire a new significance thereby. We can take as an example the concept of a "distribution function", fundamental in Roginskii's theory yet lacking physical significance in that theory, which serves to characterise the non-uniformity of a surface.

Consider a surface which is "non-uniform with respect to the heat of adsorption q". This means that the surface consists of different areas characterised by different values of q. The "distribution function with respect to the heat of adsorption q" which we shall denote by $F(q)$, where q varies over some interval between q_{min} and q_{max}, gives the fraction of the surface characterised by a given value of q. By definition

$$F(q) = ds/dq, \tag{6}$$

where ds is the fraction of the surface for which q lies between q and $q + dq$.

If ϵ_s varies over the surface, the latter will have, according to Eqn. (3), a non-uniform behaviour with respect to the heat of adsorption q even if the binding energy q^0 is constant for all points on the surface. We must remember that the value of ϵ_s, that is, the depth of the Fermi level below the conduction band in the plane of the surface, is determined by the concentration of impurities at the surface and in the bulk of the crystal. Therefore ϵ_s will vary from point to point of the surface if the impurities in the crystal are not homogeneously distributed, that is, whenever a concentration gradient of impurity exists along

the surface — the impurity can be of one and only one given kind, and does not itself take part in the act of adsorption: the only requirement is that it must be distributed non-uniformly.

For each arrangement of the impurity there will be a corresponding "distribution function" $F(q)$. In this way, the "distribution function" acquires some physical meaning. The problem was recently discussed by Peshev and the present author[7]. We shall list, as an example, some of their results.

The first example concerns the distribution function

$$F(q) = ds/dq = \text{const}, \quad (7)$$

that is, a uniform distribution of the elements of surface with respect to heat of adsorption, which can be realised by a gaussian arrangement of the impurity along the surface (around any point taken as the origin):

$$N(r) = C\exp(-r^2/r_0^2), \quad (8)$$

where $r = \sqrt{x^2+y^2}$, the coordinate axes x and y lying in the plane of the surface, and N being the concentration of impurity at the surface.

Second example. An exponential distribution function

$$F(q) = ds/dq = \alpha\exp(-\beta q) \quad (9)$$

is obtained when the impurity arrangement is parabolic:

$$N(x) = C(x - x_0), \quad (10)$$

where β and γ are uniquely related.

Thus, the various non-uniform arrangements of the impurity give rise to various "distribution functions". This is a possible interpretation of the "distribution function", but not the only possible one.

c. Active Centres

Another concept very widely used in the study of catalysis, and physically even less understood than the "distribution function" in the theory of adsorption at non-uniform surfaces, is the concept of "active centres". The term refers to specific points on the surface which support the catalytic reaction, in contrast to the remainder of the surface, which is catalytically inert.

The notion of "active centres", without specifying their physical meaning, is all that is required to construct a phenomenological theory of catalysis. This leaves obscure, however, the physical nature of such active centres. In Kobozev's theory of ensembles the active centres are identified with various combinations of catalyst atoms (pairs, groups of three, etc.), the catalyst being deposited as an amorphous phase on a catalytically inert substrate. A. A. Balandin's multiplet theory dispenses with this concept altogether. However, as a rule the concept of "active centres", devoid of any concrete physical significance, is widely adopted by students of catalysis.

According to the electronic theory[1], the catalytic activity of a surface is determined by the fraction of the total number of chemisorbed molecules which is found to be in a reactive state. The reactive molecules are those in the form of radicals or radical-ions, unlike the valency-saturated molecules, which are considered to be unreactive to a first approximation. As in other theories of catalysis, "active centres" are invoked: a molecule is in a reactive state when it is adsorbed at an "active centre". It is the binding to the "active centre" which makes the molecule reactive.

In the electronic theory, free (unsaturated) surface bonds play the role of "active" centres. These include valencies freely wandering along the surface, pointing from the surface into the bulk of the crystal, and pointing from the bulk towards the surface. Alternatively, the free valencies can be fixed (localised) at various structural defects of the surface. It can be shown that free electrons and holes in the crystal lattice play the role of unsaturated valencies. Thus, these entities fulfil the function of "active centres" in the electronic theory.

Having adopted this model for the "active centres", we should be able to predict some of their properties. Generally speaking, the centres are not immobile: they wander along the surface until they encounter chemisorbed molecules to which they become bound. This causes localisation of the centres. At the same time, the binding of the molecule to the surface becomes stronger, and the molecule is converted into a radical-ion and becomes reactive. Alternatively, the "active centre", having spent some time bound to the molecule, can break free and resume its wandering along the surface. When this happens the molecule left on the surface loses its reactivity and reverts from the radical-ion to the valency-saturated (and therefore electrically neutral) state. The concentration of "active centres" of this type on the surface is not fixed: they can be supplied from the bulk of the semiconductor (or, conversely, they can be adsorbed into the bulk) both during catalyst preparation and in the course of the reaction.

Thus, the idea of "active centres" acquires a concrete physical meaning in the electronic theory, and this clarifies their properties and their mode of operation.

d. Reversible and Irreversible Form of Chemisorption

As a further example of the way in which old facts acquire a new meaning in the light of the theory we shall consider the problem of the reversible and the irreversible form of chemisorption: the coexistence of both these forms appears to be characteristic of semiconductors.

From the point of view of the electronic theory, particles chemisorbed at a semiconductor surface can be either in an electrically charged or in an electrically neutral state. Under conditions of electronic equilibrium the relative amount of each kind is strictly fixed. However, electronic equilibrium can be disturbed in a number of instances. It is never achieved in the early stages of adsorption, and it can be destroyed during desorption. This type has been examined in detail in a recent paper by Peshev and the writer[8].

In this system, only the neutral form of chemisorbate, effectively, leaves the surface. Only later, as they become discharged, do the particles in the charged state vacate the surface. In this way, slow electronic transitions can inhibit the desorption process. If desorption of the charged form is sufficiently slow, it can be treated as irreversible. A significant increase of temperature is needed to remove the adsorbate completely from the surface.

Thus, the neutral and the charged form of chemisorption can, under certain conditions, behave as the reversible and the irreversible form respectively. This also

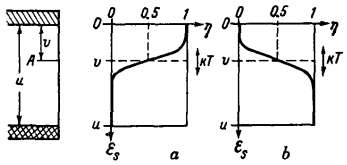

Fig. 2.

explains the occurrence of the two forms of chemisorption: it is one possible (but not the only possible) mechanism for the appearance of the two forms of chemisorption so familiar to the experimenters.

To conclude this section, we shall note that the coexistence of neutral and charged chemisorption forms on the surface is one of the crucial conclusions of the electronic theory. We must always remember, however, and this remark applies particularly to experimentalists attempting to "confirm" or "refute" the electronic theory, that under a given set of conditions practically the whole of the particles chemisorbed on the surface will be found in the neutral state (or alternatively in the charged state). Instances in which both forms are present in comparable amounts are quite rare.

This should be clear from Fig. 2, which shows, on the basis of Fermi statistics, the variation of the fractional amount of the charged form, η, with the position of the Fermi level, ϵ_s, under conditions of electronic equilibrium for acceptor particles (Fig. 2*a*) and for donor particles (Fig. 2*b*). A is the localised level due to the chemisorbed particles. We can see that the quantity η differs appreciably from zero or from unity only when the Fermi level lies fairly close to the level A (within a distance smaller than or of the same order as kT).

Thus, it is possible to convert the neutral (reversible) form of chemisorption into the charged (irreversible) form or vice versa by shifting the Fermi level, that is, by varying the conditions or the previous history of the sample.

3. SOME PREDICTIONS WHICH HAVE BEEN CONFIRMED

a. Relationship between Catalytic Activity and Electrical Conductivity

Turning now to the predictions of the electronic theory which have already been put to experimental test, we must, of course, point out first of all the relationship between the catalytic activity and the electrical conductivity of a semiconductor. The correlation between these two characteristics was predicted theoretically[9] as early as in 1950, when no experimental work of any kind existed in this field.

At the present time we can refer to a whole series of researches in which this correlation has been experimentally observed: many workers have measured the electrical conductivity and the catalytic activity of differently treated samples, and have observed a direct or an inverse relation between these two characteristics of the semiconductor on going from sample to sample.

We shall not enumerate all these investigations: they are quite well known. We shall only refer to a few of them to illustrate the point. Keier and coworkers[10] studied the oxidation of carbon monoxide on specimens of nickel oxide containing different amounts of lithium added as an impurity. They established an unmistakable inverse relationship between activity and electrical conductivity: the higher the initial conductivity, the lower was the activity of the material. Rienäcker[11] studied the decomposition of dinitrogen monoxide on the same semiconductor, nickel oxide, doped with different amounts of aluminium. He found that the electrical conductivity and the activity varied in the same sense. The same result was obtained by Heckelsberg and coworkers[12] in their study of the hydrogen–deuterium exchange reaction on zinc oxide containing various impurities.

b. Relationship between Catalytic Activity and Work Function

The thermionic work function is another parameter which physically characterises a semiconductor and which, according to the electronic theory, should be related to the catalytic activity even more directly than the electrical conductivity.

The electrical conductivity is determined by the value of ϵ_v (the depth of the Fermi level below the conduction band in the bulk of the crystal, see Fig. 1), whereas the adsorption properties and the catalytic activity are determined by the quantity ϵ_s (the depth of the Fermi level at the surface). There is a definite relationship between ϵ_v and ϵ_s, but this can often be distorted or obscured, thus upsetting the correlation between electrical conductivity and activity. On the other hand, the work function φ (see Fig. 1), ignoring the dipole contribution δ and to the accuracy of the constant term χ, is equal to ϵ_s by definition ($\varphi = \epsilon_s + \chi + \delta$). It is therefore unequivocally related to the adsorption properties and to the catalytic activity.

A correlation between catalytic activity and work function, that is, a variation in the same or in the opposite sense between these two quantities, was predicted in theoretical papers[2] published in 1948–1950. Many papers published since that date have described experimental confirmations of this theoretical prediction: we shall not attempt to list them comprehensively here. Two examples will suffice. Margolis and coworkers[13], in their study of the oxidation of propene on copper(II) oxide doped with various impurities, observed an inverse relationship between activity and work function: the materials with the lowest work function were the most active in causing complete oxidation. A similar correlation was found by Zhabrova and coworkers[14], who investigated the dehydrogenation of isopropyl alcohol on variously doped specimens of zinc oxide.

c. Changes in Work Function and Electrical Conductivity upon Adsorption

When discussing the relationship between the work function and the electrical conductivity of a semiconductor on the one hand, and between the work function and the adsorption properties and catalytic activity on the other hand, we often have in mind the changes in work function and electrical conductivity induced by adsorption itself, or occurring in the course of a catalytic reaction, rather than just a correlation between these two quantities among a number of differently prepared samples. The effect is caused by

the charging of the surface upon adsorption, leading to a shift of the Fermi level and a change in the concentrations of free electrons and holes in the layer of semiconductor immediately below the surface.

The charging of adsorbed particles resulting from the localisation of free electrons or holes from the crystal lattice onto those particles, was demonstrated theoretically as long ago as in 1948–1951 [2,9,15]. The effect has now been studied experimentally in fair detail on a variety of systems. Experimentalists often use it to establish the nature (acceptor, or donor) of the adsorbate when the nature of the adsorbent is known (n- or p-type semiconductor). It can also be used to establish the nature of the adsorbent if the nature of the adsorbate is known.

We shall not attempt to review all these experimental investigations. They are very numerous, and quite well known. Indeed, we must beg the indulgence of the readers for dwelling on familiar material in this section of the paper.

d. The Photoadsorption Effect

The photoadsorption effect must be mentioned among those instances in which theory did not follow experiment, but rather led the way. The effect can be positive or negative: an increase or a decrease in the adsorption properties of the material under the influence of light. It was discovered, and originally investigated, by Terenin and coworkers, and by Hedwall, in the 1930's. However, the factors which determine the sign of the effect remained obscure for many years.

The first attempts [4] to set up a theory of the photoadsorption effect, in 1958, showed that the sign of the effect depends, under otherwise constant conditions, on the previous history of the specimen, and can be changed by suitable pretreatment. Shortly afterwards, Fujita and Kwan [16], working in Japan, were able to demonstrate sign inversion for oxygen on zinc oxide by controlling the departure from stoichiometry of the sample.

Further theoretical work by the writer and Karpenko [17] showed that the sign of the effect is determined by the position of the Fermi level within the crystal, ϵ_v, and by the bending of the bands, V_s (see Fig. 1). Fig. 3, reproduced from that paper [17], shows the region of possible values of ϵ_v and V_s compatible with a Boltzmann distribution of free carriers throughout the crytal for acceptor particles on an n-type semiconductor (for example O_2 on ZnO). The straight line AA divides this region into areas of positive and negative effects, denoted by different cross-hatching on the Figure. The segment v (compare Fig. 1) indicates the position in the energy spectrum of the crystal of the localised surface level corresponding to the adsorbate particles of the kind being considered; the segment V_s characterises the initial bending of the bands, existing in the absence of any adsorbed particles on the surface and therefore caused by surface states arising otherwise than by adsorption; u denotes the width of the forbidden gap between the bands. It is evident that we can pass from the region of positive to the region of negative photoadsorption effect, and vice versa, by shifting the Fermi level ϵ_v, or by changing the band bending V_s, or by changing both parameters at the same time.

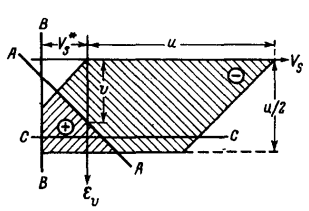

Fig. 3.

In the light of this theoretical prediction, it is relevant to mention some recent results obtained by Kwan [18], who studied the effect by investigating the adsorption of oxygen on zinc oxide containing lithium or aluminium. In the former a positive effect was observed, in the latter a negative, as was indeed to be expected on the basis of Fig. 3, since the replacement of an acceptor impurity (lithium) by a donor (aluminium) must always move the Fermi level upwards. Referring to Fig. 3, we see that this may cause a transition from the region of positive photoadsorption to the region of negative photoadsorption.

Also in agreement with Fig. 3 are some recent results of Haber and Kowalska [19], who investigated the same system (oxygen on zinc oxide). Oxidation of the surface was found to change the effect from positive to negative, as required by Fig. 3. This is because oxidation of the surface is accompanied by an increase in V_s, which causes a shift from left to right in Fig. 3 (for example, from the positive effect towards the negative effect region).

e. The Electroadsorption Effect

We shall consider one other phenomenon predicted theoretically in 1958 and experimentally observed only very recently. This is the phenomenon for which we have suggested the term "electroadsorption effect".

The theory leads us to expect a change in the adsorption properties of a semiconductor upon application of an external electric field normal to the adsorbent surface. This effect, resulting from the displacement of the Fermi level under the influence of the field, was computed by Sandomirskii and the writer [20] for a semiconductor located between two condenser plates and therefore retaining electrical neutrality when the field is applied. For the field effect technique, when the semiconductor under study acts as one of the electrodes and acquires an induced charge upon application of the field, the calculation was carried out by the writer in cooperation with Baru [21].

The field effect method, though widely used in semiconductor studies and ideally suited to the investigation of the role of electronic factors in chemisorption and catalysis, is only just beginning to make its first tentative steps in catalysis laboratories, owing to a number of specific practical difficulties. Thus, the use of single crystals (which is the rule in field effect experiments) makes it difficult if not altogether impossible to carry out direct adsorption measurements. The extent of adsorption has to be inferred indirectly from the change in surface conductivity. The electrical charge in the gas phase, which appears at not too low pressures and high enough fields, is another complication. Great care is needed to ensure that the new effect being sought is not confused with trivial electrochemical effects.

Among the experimental studied we can single out that of Lyashenko and coworkers[22], and also that of Mikheeva and Keier[23], who actually observed the expected change in the adsorption properties of the surface under the influence of an external electrical field (adsorption of acceptor and of donor gases on germanium). The former used a direct adsorption method (by monitoring pressure changes in the adsorption volume), the latter relied on changes in electrical conductivity.

4. SOME PREDICTIONS STILL AWAITING CONFIRMATION

We have now reached the final, yet the most important, section of the paper. We shall examine a numer of predictions implicit in the electronic theory which have not yet been fully formulated, or subjected to experimental test.

a. Role of an External Electric Field

We must deal first of all with the phenomena stemming from the influence of an external electric field on the properties of the surface.

The field effect method, already considered above, can be used as a new and very sensitive procedure for determining the surface coverage of the charged form of chemisorption, and can also be used to measure adsorption on single crystals. The electric circuit for the field effect method is shown in Fig. 4*a*: the current i is measured as a function of the field strength E. The specimen is shown cross-hatched in Fig. 4*a*.

Fig. 4*b* shows some typical field effect curves (variation of the surface conductance σ with E). The heavy line corresponds to a specimen in a vacuum: the thin line corresponds to the same specimen in a gaseous medium (the diagram refers to conditions when the adsorbent is an n-type semiconductor and the adsorbate behaves as an acceptor). Assume that we are at point A on the heavy curve; admission of gas takes us to point B, showing a fall in conductance from the initial value σ_0 to σ_1. We now change the field by an amount ΔE (from E_0 to $E_1 = E_0 + \Delta E$), in such a way as to travel along the thin curve from point B to point C. This restores the conductance to its initial value σ_0.

From the value of ΔE we can arrive at the amount of charge gained by the surface as a result of adsorption. We have

$$\Delta E = -(4\pi e/\varkappa) N^-, \qquad (11)$$

where N^- is the surface concentration of chemisorbed particles which are in the uncharged state, e is the absolute value of the electronic charge, κ is the dielectric constant of the gaseous medium.

Thus, from the "compensating" field ΔE and from the dependence of ΔE on E_0 we can determine both the surface coverage by the charged form, N^-, and the "electroadsorption effect", that is, the change in the above coverage brought about by the external field (N^- as a function of E_0):

$$N^- = N^-(E_0).$$

This simple "compensation method" is the most direct way of measuring the effect of an external field on the adsorption properties of the surface.

As regards the effect of the field on the catalytic activity (acceleration or inhibition of the catalytic reaction by the applied field), an effect for which we propose the name "electrocatalytic effect", it also follows from the theory and for the same reasons, but it still remains a theoretical prediction awaiting experimental confirmation. Experimental studies of the effect of an external field on the chemisorption and catalytic properties of a semiconductor surface are only just beginning. We may hope that they will expand in the coming years.

b. Role of a Magnetic Field

A magnetic field should have an effect similar to that of an electric field. Consider a plane-parallel slab of a semiconductor to which are simultaneously applied an electric and a magnetic field, parallel to the adsorbing surface but mutually perpendicular (see Fig. 5). Due to the Hall effect one of the surfaces will be depleted of current carriers whilst the other is enriched by the same factor. As a result, the adsorption capacity of the specimen as a whole becomes greater, as we shall proceed to show.

Let N_0 be the concentration of chemisorbed particles on each of the surfaces in the absence of a magnetic field, and ΔN_1 and ΔN_2 be the increments caused by the magnetic field on the two adsorbing surfaces respectively. As can readily be shown[21] we have

$$\left.\begin{aligned} \frac{\Delta N_1}{N_0} &= \eta_0\left[\exp\left(-\frac{\Delta V_s}{kT}\right) - 1\right], \\ \frac{\Delta N_2}{N_0} &= \eta_0\left[\exp\left(+\frac{\Delta V_s}{kT}\right) - 1\right], \end{aligned}\right\} \qquad (12)$$

where $-\Delta V_s$ and $+\Delta V_s$ are the changes in surface potential V_s (see Fig. 1) induced by the magnetic field on the corresponding surfaces, and η_0 is the relative amount of the charged form of chemisorption on the surface in the absence of the magnetic field.

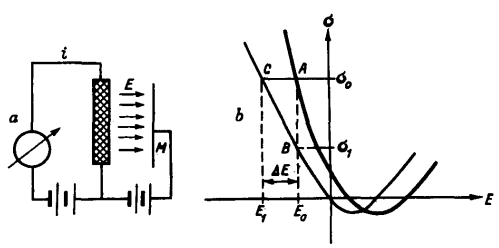

Fig. 4.

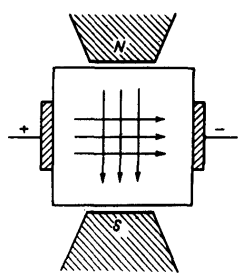

Fig. 5.

Clearly,

$$\left.\begin{array}{ll} \text{if} & \frac{\Delta N_1}{N_0}<0, \text{ then } \frac{\Delta N_2}{N_0}>0, \\ \text{if} & \frac{\Delta N_1}{N_0}>0, \text{ then } \frac{\Delta N_2}{N_0}<0. \end{array}\right\} \quad (13)$$

The relative change in the adsorption capacity of the specimen as a whole becomes, from Eqn. (12):

$$\frac{\Delta N}{N_0}=\frac{\Delta N_1}{N_0}+\frac{\Delta N_2}{N_0}=4\eta_0 \sinh^2\frac{\Delta V_s}{kT}\geqslant 0. \quad (14)$$

The increased adsorption capacity can be detected not by direct adsorption measurements, which would be very difficult under the conditions of this experiment, but from the changes in electrical conductivity occurring during adsorption. The change should be more pronounced in the presence than in the absence of a magnetic field (provided, of course, that all the other conditions remain the same).

It can be shown that the magnetic field will increase, at the same time as the adsorption capacity, also the catalytic activity towards any catalytic reaction which proceeds by an electronic mechanism.

c. Role of Illumination

Let us return to the photoadsorption effect, already discussed above. We shall define the magnitude of the effect by the quantity

$$\Phi=\frac{\Delta N}{N_0}, \quad (15)$$

where N_0 is the concentration of adsorbed particles in the dark, ΔN is the increment brought about by the illumination. The quantity Φ is the relative change in the adsorption capacity of the surface under the influence of light. Obviously, Φ can be positive (photoadsorption) or negative (photodesorption).

Fig. 6 shows the theoretical curve for the variation of the photoadsorption effect Φ with position of the Fermi level in the bulk of the crystal ϵ_v (see Fig. 1). The Figure, reproduced from a paper by the writer and Karpenko[24], refers to acceptor-like adsorbed particles. The quantity u in Fig. 6 denotes the width of the forbidden gap between the bands, V_s is the bending of the bands, v is the depth of the localised energy level A due to the chemisorbed particle below the conduction band. The meaning of the symbols used is made clear by comparing Figs. 6 and 1.

It is obvious from Fig. 6 that we must expect a correlation between the magnitude of the photoadsorption effect and the initial dark conductivity of the semiconductor, determined by ϵ_v: the greater ϵ_v, the smaller will be the electronic conduction and the greater the hole conduction in the semiconductor. We see that if all other conditions are equal the algebraic value of the photoadsorption effect should be higher, the smaller the dark conductivity of the specimen. This is true, as can also be seen from Fig. 6, of n- and p-type semiconductors alike: the former corresponds to the upper half of Fig. 6 ($\epsilon_v < u/2$), the latter to the lower half ($\epsilon_v > u/2$). It would be interesting to test this prediction experimentally. Equally interesting would be a study of the photoadsorption effect in conjunction with the field effect, that is, a study of the combined effects of light and of an external electric field on a semiconductor. This is because an external field allows the band bending V_s to be varied over very wide limits without affecting the value of ϵ_v. In other words, a change in the intensity of the external field results in a horizontal movement in Fig. 3 (for example, along the line CC), and it is evident from Fig. 3 that this may lead to a change in the sign of the photoadsorption effect. We must expect, therefore, that sometimes either photoadsorption or photodesorption will occur on a particular specimen under a constant set of conditions, according to the magnitude and direction of the external electric field applied to the specimen.

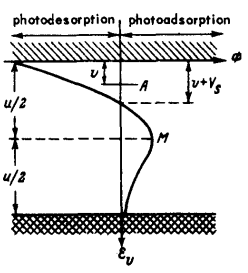

Fig. 6.

d. Role of Impurities

An electric field, a magnetic field, and illumination are factors which affect the chemisorption and catalytic properties of a semiconductor, all things considered, by the same mechanism. They bring about a change in the concentration of the electron or hole gas at the crystal surface. This is enough to explain the mechanism of their influence on the chemisorption properties and on the catalytic activity of a surface.

Impurities added to the bulk of the crystal are yet another factor involving the same mechanism. This statement applies to impurities contained in the crystal in a state of atomic subdivision; impurities forming a separate phase are, of course, excluded. Impurity effects on the activity of a catalyst (catalyst promotion or poisoning) have been known for a long time; they are now well characterised from the point of view of experiment as well as theory (including the electronic theory).

The effect of impurities on the adsorption properties of a surface has received much less attention. We refer to impurities added to the bulk of the crystal and not wholly residing on the surface. Impurities deposited on the surface can act as adsorption centres, or, conversely, they can block existing adsorption centres. We are not concerned here with this simple mechanism of impurity action, but with the influence of impurities on the properties of the surface through their effect on the electronic state of the system as a whole, not involving direct contact between the impurity and the adsorbate.

The electronic theory predicts a decrease in the adsorption capacity of the surface for acceptor gases, and an increase in the adsorption capacity for donor gases, when an acceptor impurity is added to the crystal. A donor impurity should have the opposite effect. It must be noted, however, that a given impurity will behave as an acceptor or as a donor not only according to its own nature, but also according to the nature of the crystal to which it is

added and to the way in which it is added to the host crystal. By the same token, adsorbed molecules behave as acceptors or donors according to the nature of the centres on which they are adsorbed as well as to their own nature. The unambiguous criterion of the acceptor or donor role of an impurity is the way in which it affects the electrical conductivity (whether it increases or decreases the electron and the hole contributions to the conductivity). The unambiguous criterion of the acceptor or donor role of an adsorbed molecule is its effect on the work function (whether it increases or lowers it, respectively).

If we compare the adsorption of a particular gas under otherwise constant conditions on differently doped specimens of a given semiconductor we expect to find a family of adsorption isotherms such as those shown in Fig. 7, which are numbered in order of increasing (or decreasing) concentration of impurity in the crystal.

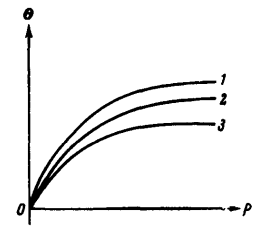

Fig. 7.

At the same time, we should expect a correlation between the adsorption capacity and the electrical conductivity, similar to the correlation which exists between catalytic activity and electrical conductivity (see Section 3, a). For an *n*-type semiconductor the adsorption capacity towards an acceptor gas should change in the same sense as the electrical conductivity and the adsorption capacity towards a donor gas should change in the opposite sense. For a *p*-type semiconductor the reverse is true.

Of course, such a correlation can be expected only if the impurity added to the bulk of the semiconductor has no effect at all on the system of surface states. The correlation between electrical conductivity and work function can be used as a criterion that such is the case.

Impurities which affect the relative amounts of the neutral and the charged form of chemisorption in the surface affect *ipso facto* the relative proportions of reversible and irreversible chemisorption. We can expect, therefore, that different amounts of irreversibly adsorbed gas will be retained, on pumping, by specimens with different impurity concentration, even if the nature of the gas and all other conditions are constant.

An experimental study of the influence of impurities dissolved in the semiconductor upon the adsorption properties of the semiconductor surface would be very interesting. Such a study, however, would meet with a number of practical difficulties. One would have to ensure that the impurity was entirely within the semiconductor, and that none had been retained on the surface, in order to observe this effect in a "pure" form.

e. Semiconducting Films on Metals. Role of Disperseness

We shall discuss the results of yet another theoretical piece of work susceptible to (but still awaiting) experimental test. The writer has investigated, with Sandomirskii and Kuznetsov[25], the adsorption and catalytic properties of a thin semiconductor film covering a metal surface. It is well known that many metals are covered, under most conditions, with a film of a binary compound, that is, they are clad with a semiconductor coating. Statements as to the catalytic action of a metal often relate, in fact, to the catalytic action of this semiconductor film. This has been stressed on many occasions by Roginskii[46] and others. If, however, the thickness of the film is small compared with the dielectric screening length of the semiconductor, then the adsorption and catalytic properties can be shown to depend on the thickness of the film and on the properties of the metal substrate: the film behaves as if it were "translucent" to the characteristics of the metal.

In most practical instances, the semiconductor film arises as a result of oxidation of the metal, and its thickness can often be controlled to some extent. The film of copper(I) oxide which grows on a copper matrix is a typical example. By varying the thickness of the coating, it is possible to apply a measure of control on the adsorption capacity, the catalytic activity, and the selectivity of the specimen. This effect is due to the fact that the position of the Fermi level in a film of this type depends on the thickness of the film. It would be interesting to study the adsorption and catalytic properties of a semiconducting film on a metal, and their changes, during growth of the film.

There is another effect which can be said to have the same origin: the variation of the specific (that is, calculated per unit surface area) adsorption capacity and catalytic activity of very finely divided materials with degree of dispersion (or grain size). This effect was studied theoretically by Kogan[27] four years ago. It offers yet another topic for experimental work, yet another incursion of theory into experiment.

f. Relationship between Differential Heat of Adsorption and Work Function

We shall return now to formula (3), which expresses the variation of the differential heat of adsorption q with the position of the Fermi level ϵ_s at the surface of the crystal, and also to Fig. 1. It can be seen from the diagram that the electron work function, labelled φ in Fig. 1, is related to the Fermi level ϵ_s, by definition, as follows:

$$\varphi = \varepsilon_s + \chi + \delta, \qquad (16)$$

where δ is the so-called "dipole contribution" to the work function (that is, the additional potential step at the crystal surface arising from the polarisation of the adsorbed molecules), whilst χ is a constant which characterises the lattice of the adsorbent (the affinity of the ideal lattice for a free electron), so that the differential heat of adsorption q is unambiguously related to the work function φ if we ignore the dipole contribution δ as is commonly done.

Thus, a correlation between the differential heat of adsorption and the work function can be expected under certain conditions. As the surface coverage is progressively increased the differential heat and the work function should vary together and in the same sense if the adsorbate behaves as a donor, or in the opposite sense if it behaves

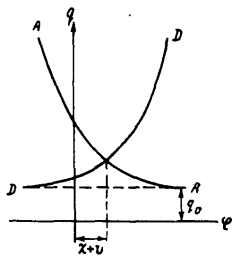

Fig. 8.

as an acceptor. The two cases correspond to the upper and lower sign in formula (3) respectively. Fig. 8 is an idealised plot of the relationship between q and φ for the adsorption of donor (curve DD) and of acceptor species (curve AA) on the assumption that $\delta = 0$.

This is yet another theoretical prediction amenable to experimental test.

We must now bring to a close this list of predictions stemming from the theory and ready to be handed over to the experimental scientists in the hope of enlisting their active interest. This is not because the list is now complete but rather because it would be unrealistic to attempt to make it complete in the space of one article.

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In conclusion, I would like to deal with a number of criticisms which could be levelled at the present article, and argue with an imaginary opponent. We can forsee three kinds of criticism (this is the last of the "theoretical predictions").

Firstly, it could be argued that the suggested experiments are difficult, and perhaps even unrealistic, for a number of reasons. To this I would reply that the present paper does not propose any definite procedures: we have only put forward the ideas of a few experiments with no other aim than to bring them to the attention of the experimental scientists. The present list of theoretical predictions, though idealised and curtailed, is a list of the points of arrest in the development of the theory where the theoretician would like to meet the experimenter.

Secondly, a list of facts which the theory has so far failed to explain could be contrasted with the facts which have been interpreted more or less successfully by the theory. There may well be unexplained facts, and more may come to light in increasing numbers. But these facts are the fertile soil in which the theory can continue to grow, improve, and perhaps even remodel itself in parts.

Thirdly, and lastly, facts allegedly in conflict with the theory could be put forward. Of course, theory must be judged by experiment. We always begin with experiment and always come back to it. However, as experiment itself shows, the experimental investigations which "refute" the electronic theory (and also, indeed, some of those which "confirm" it) should be treated with greater caution. Often these investigations, despite the claims of their authors, "refute" nothing and "prove" nothing, being the outcome of an insufficiently critical reading of the theory.

What, then, can the theoretician and the experimenter ask of each other when they meet on the domain of catalysis? The experimenter cannot, of course, expect from the electronic theory predictions of the numerical values of various physical quantities: he can expect the theory to discover the physical mechanism of the observed rules, and to predict new rules and relationships. We must therefore remember that in the field of catalysis (as indeed, in every other field) reality is immeasurably more complex than any theory and never ceases to challenge our understanding. As for the theoretician, he has the right to expect from the experimenter not casual observations but experiments which put a clear question to Nature and elicit an answer.

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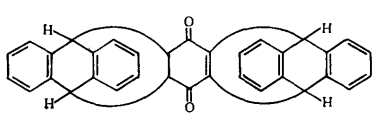
STEREOCHEMISTRY OF HYDROGENATION AND HYDROGENOLYSIS

E.I. Klabunovskii

Optically active compounds and compounds whose molecules have a rigid three-dimensional configuration may prove extremely useful in the study of the mechanism of catalysis and the structure of the active surface of catalysts. The advantages of catalytic studies of this kind arise because the initial molecules has a definite well known configuration and it is possible to construct stereochemical models for the intermediate complexes, to follow the stereochemical reaction pathways, and to obtain information about the structure of the active surface of the catalyst.

Such studies are being made both to investigate the geometry of the catalyst surface, using reactions of molecules with a complex three-dimensional structure, and to elucidate the configurational and energy interactions between the groups of the optically active compounds adsorbed on the surface.

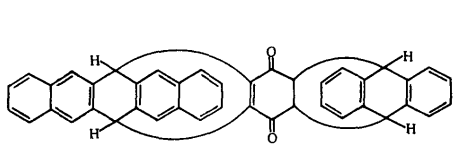
The first approach to the study of the active surface of catalysts has been achieved by hydrogenating triptycene derivatives[1] such as 2,3(9,10-anthrylene)-5,6-(9,10-anthrylene)-2-cyclohexene-1,4-dione (I), for example:



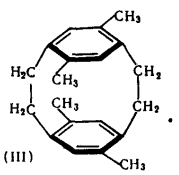
(I)

The hydrogenation of the C=C bond in the central ring of this compound occurs at an appreciable rate on a nickel catalyst even at 45°.[1] The preservation of the rigid structure of the molecule during the catalytic process, which excludes any appreciable deformation or reversal of the configuration by an S_N2 mechanism, makes it possible to construct stereochemical models of the active centre. Since chemical valence forces are of short range, the molecules are in contact with the catalyst via the reacting C=C atoms, which determines the orientation of the molecule during catalysis. The edgewise orientation on the surface is excluded in this case by the structure of the molecule and therefore it is necessary to postulate a planar disposition of the central ring on the (111) plane of the nickel crystal. Since the molecule has a complex three-dimensional structure, it cannot lie flat on this plane and it must be assumed that the correct orientation of such a molecule on the centre requires a projecting centre bounded by the (111) plane and adjacent to a number of "hollows" where the non-reacting parts of the molecules are located. On the basis of the actual dimensions of the molecular model, the height of the projecting centre in an optimum catalyst of this kind must be not less than 4.30 Å.

On catalysts with both "rougher" and more "even" surfaces the reaction of such a compound is hindered because of the reduced probability of occurrence on the surface of centres corresponding to the structure of the reacting molecule. Equally, the reaction rate may be reduced also because of an increase in "catalytic difficulties" as a result of an increase in the complexity of the three-dimensional structure of the molecule, for example when instead of compound (I) compound (II) is hydrogenated:



(II)



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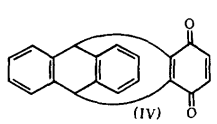
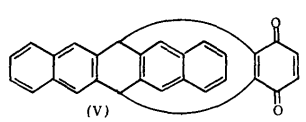
It is interesting that tetramethyl[2,2]paracyclophane (III)[2] is not hydrogenated at the usual temperature and pressure on 10% Pd/C catalysts or PtO_2. In the general case breakdown of the coplanarity of the molecule hinders hydrogenation. However, when the non-coplanar part of the molecule is not in immediate contact with the catalyst, as, for example, in the hydrogenation of triptycenequinone (IV) and dibenzotriptycenequinone (V), the rates of hydrogenation (1 atm, 45°) are almost indistinguishable[3].



(IV)



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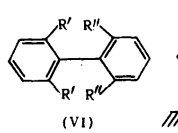
The structure of the molecule is the decisive factor in the catalytic reaction and when the structure is sufficiently complex and rigid, preventing the contact of the molecule with the active catalyst surface, the reaction cannot be achieved. For example, the biphenyl derivatives (VI)[4] are not hydrogenated as a result of the hindrance of the catalysis by the substituents R′ and R″ [structure (VII)], while hydrogenation of triptycene derivatives, although small, is in fact possible[3]:



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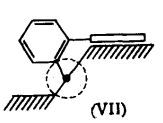

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The study of the catalytic reactions of homologous compounds with a complex three-dimensional configuration allows the statistical distribution of the active catalyst centres with respect to size to be found in principle[5].

Another approach which makes it possible to estimate not only the geometry of the active catalyst surface but also to take into account the energy interaction between the catalyst and various functional groups in the substrate molecule is the study of the mechanism of the hydrogenolysis of optically active compounds[6]. In this reaction the bond $\overset{*}{C}-X$ at the asymmetric carbon atom of the molecule (VIII) is ruptured with formation of the compound (IX); since the reaction involves the asymmetric centre, this

30. F.Romero-Rossi and F.S.Stone, "Deuxième Congrès International de Catalyse", Paris, 1960, Paper No.70.
31. G.M.Schwab and J.Block, Z.phys.Chem.(Frankfurt), 1, 42 (1954).
32. G.Parravano, J.Amer.Chem.Soc., 74, 1194 (1952); 75, 1448, 1452 (1953).

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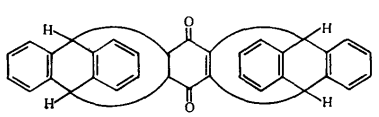
STEREOCHEMISTRY OF HYDROGENATION AND HYDROGENOLYSIS

E.I. Klabunovskii

Optically active compounds and compounds whose molecules have a rigid three-dimensional configuration may prove extremely useful in the study of the mechanism of catalysis and the structure of the active surface of catalysts. The advantages of catalytic studies of this kind arise because the initial molecules has a definite well known configuration and it is possible to construct stereochemical models for the intermediate complexes, to follow the stereochemical reaction pathways, and to obtain information about the structure of the active surface of the catalyst.

Such studies are being made both to investigate the geometry of the catalyst surface, using reactions of molecules with a complex three-dimensional structure, and to elucidate the configurational and energy interactions between the groups of the optically active compounds adsorbed on the surface.

The first approach to the study of the active surface of catalysts has been achieved by hydrogenating triptycene derivatives[1] such as 2,3(9,10-anthrylene)-5,6-(9,10-anthrylene)-2-cyclohexene-1,4-dione (I), for example:



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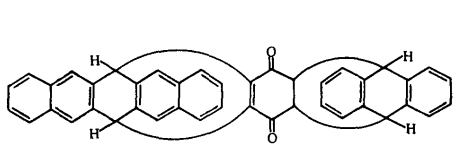

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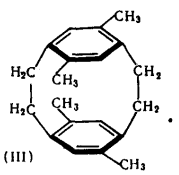

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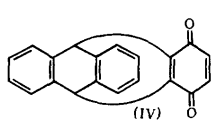

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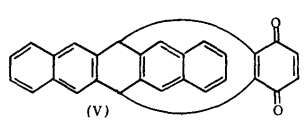

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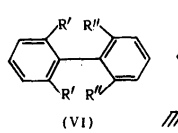

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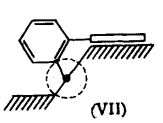

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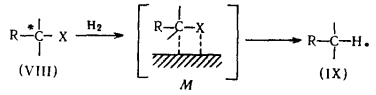
Another approach which makes it possible to estimate not only the geometry of the active catalyst surface but also to take into account the energy interaction between the catalyst and various functional groups in the substrate molecule is the study of the mechanism of the hydrogenolysis of optically active compounds[6]. In this reaction the bond $\overset{*}{C}-X$ at the asymmetric carbon atom of the molecule (VIII) is ruptured with formation of the compound (IX); since the reaction involves the asymmetric centre, this

compound can remain either optically active (with retention of inversion of the initial configuration) or lose activity as a result of racemisation:



(VIII) M (IX)

A heterogeneous catalyst, on the surface of which an intermediate state *M* is established, makes its own contribution to the stereochemistry of the complex. On general grounds, it may be expected that the introduction of an interface lowers the symmetry of the system and therefore one would expect retention of the configuration of the reacting molecule. However, experiment shows that reactions often take place with inversion of configuration. The use of optically active compounds in catalysis provides valuable information about the nature of the intermediate state: whether it is symmetrical or asymmetric, and to what extent the non-reacting parts of the molecule are involved in the intermediate complex (for example, by comparing the reactions of a number of homologues). Racemisation at a centre not participating directly in the reaction would indicate that adsorption of the substituents plays a role; in conjunction with isotope exchange, it can provide additional information about the details of the mechanism of the reaction on the catalyst surface.

The number of systematic investigations of the mechanism of catalysis using optically active and sterically complex compounds is so far inadequate and only recently has this field been developed vigorously, particularly by Japanese investigators who have published a series of experimental papers and brief reviews[7], which are of considerable interest from the viewpoint of the stereochemical relations between the configuration of the reacting molecule and the geometry of the catalyst surface. Unfortunately, so far these data are only qualitative but their complete review is nevertheless desirable (up to 1965 inclusive).

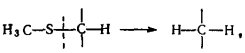
The studies in this field, which were begun by Bonner and coworkers as early as 1952 and then continued by Mitsui, Imaizumi, and others[7], developed on the basis of the hypothesis of the electronic nature of catalytic reactions, the latter being divided into several types depending on whether their mechanisms on the catalyst surface are S_N1, S_N2, or S_Ni. A detailed study has been made of the effect of the structure of the reacting optically active molecule on the type of mechanism and the effect of the nature of the catalyst (mainly Raney nickel and palladium deposited on carriers have been studied).

Extensive experimental data have been accumulated, which in most cases make it possible to establish without ambiguity the mechanism of hydrogenolysis and to draw certain general conclusions concerning the stereospecifity of the action of active catalyst centres.

Hydrogenolysis and hydrogenation of oxygen-containing and other compounds have been widely studied by Mitsui, Imaizumi, and a number of other workers[8,9], who showed that the steric requirements of the reacting molecule have a considerable influence on the rate and mode of reaction.

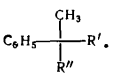
Bonner[10] was the first to use extensively optically active compounds for the investigation of the mechanism of desulphuration. Optically active sulphides, sulphoxides, and sulphones were initially studied as compounds which are firmly chemisorbed on the catalyst surface. The study of the hydrogenolysis of such compounds were also of considerable practical interest for the understanding of the mechanism of the desulphuration of petroleum and many other compounds.

Earlier such studies of the hydrogenolysis of the C–S bond concerned carbohydrates, biotin, and amino-acids, but they were confined to the investigation of hydrogenolysis by a mechanism in which a symmetrical optically inactive product is formed,

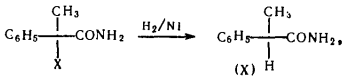


which meant that steric factors were not investigated. However, the reaction proved to be very sensitive to the three-dimensional structure of the substrate. For example, steric hindrance in hydrogenolysis is shown by the greater difficulty of the hydrogenolysis on nickel of phenylthiodiphenylacetic acid compared with the methylthio-compound, etc.[8] Bonner's studies, which were initially undertaken to elucidate the special case of the desulphuration mechanism (hydrogenolysis of the C–S bond), served as a basis for the development of a hypothesis concerning the mechanism of the hydrogenolysis of C–O, C–Cl, and C–N bonds; although formal, this hypothesis fairly correctly reflects the essential features of the processes.

The technique used to study hydrogenolysis is simple. The hydrogenolysis is usually carried out at atmospheric or elevated pressure in boiling ethanol over a period of 1–5 h in the presence of a 2–10-fold excess of catalyst. After the reaction the catalyst is filtered off and the optical activity of the reaction products is studied. Since it is easy to prepare in an optically pure form and has a benzyl group, atrolactic acid, and its derivatives are used as model compounds in most investigations; they have the general formula:



In his initial studies Bonner[10,11] investigated the hydrogeneolysis of the optically active amides of phenylpropionic acid derivatives containing sulphide, sulphinyl, or sulphonyl groups:



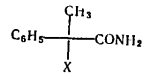
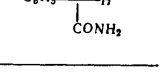
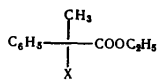
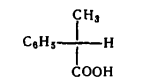
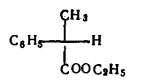
(X)

where X = SC_6H_5, SOC_6H_5, or $SO_2C_6H_5$. These compounds showed the following unusual types of behaviour (see Table 1).

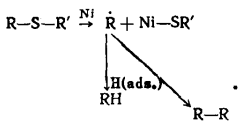
1. The phenylthio-derivative (X = SC_6H_5) gives rise to a completely racemic amide, the loss of optical activity being due to the stereochemical course of the reaction and not secondary racemisation of the amide formed, since under the experimental conditions the optically active compound (X) is racemised only to the extent of 20%.

2. The hydrogenolysis of the optically active sulphoxides (X = SOC_6H_5)[11] also leads to the racemic propionamide (X), which indicates the similarity of the mechanisms of the

TABLE 1. Catalytic hydrogenolysis of sulphur-containing optically active compounds on a Raney nickel catalyst (at 78° in ethanol at atmospheric pressure).

Initial compound			Product				
structure	X	configuration, $[\alpha]_D$	structure	$[\alpha]_D$	optical activity, %	Change in configuration	Type of mechanism	Refs.
	$-SC_6H_5$ $-SOC_6H_5$ $-SO_2C_6H_5$	I(+)$_C$(+)$_S$]; +18.7 I(+)$_C$(−)$_S$]; +55.5 I(−)$_C$(−)$_S$]; −203 I(−)$_C$(+)$_S$]; −53.2 −69.8		0 0 −28.5	0 0 90	rac. » inv.	S_N1 S_N1 S_N2	10,11 11 10,11
	$-SC_2H_5$ $-SC_6H_5$ $-SC_6H_4CH_3$ $-SO_2C_6H_4CH_3$ $-SO_2C_6H_4CH_3$	D(+) 4.11 D(+) 130.9 D(−) 18.73 D(−) 5.39 D(−) 15.5 D(−) 3.22		−0.23 −0.35 0	0.24 0.35 0	rac. » »	S_N1 $+S_N2$ То же S_N1	16 16 15
				L-(−) 20.4 L-(−) 51.0 L-(−) 18.8	81 » 75	inv. » »	S_N2 S_N2 S_N2	15 10,11 15
3-Ethylthio-3α,9α-epoxy--11-oxocholanoic acid		+100	3α,9α-epoxy-11-oxocholanoic acid	+88.1		no change	S_Ni	18

desulphuration of these compounds to the thoroughly investigated mechanism of the hydrogenolysis of sulphides[12-14], which is of the dissociative free-radical type:

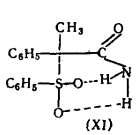


The study of the sulphoxide (X = SOC_6H_5) is complicated by the fact that this compound has two asymmetric atoms (carbon and sulphur) and forms diastereoisomers:

I(+)$_C$(+)$_S$]; I(+)$_C$(−)$_S$]; I(−)$_C$(+)$_S$]; I(−)$_C$(−)$_S$].

However it has been shown[11] that all the stereoisomers give the racemic amide (X) on hydrogenolysis.

3. The hydrogenolysis of the optically active sulphone (X = $SO_2C_6H_5$) proceeds with the retention of up to 90% of the optical activity but with inversion of the configuration. The hypothesis that this behaviour may be accounted for by the structure of the substrate molecule, cyclic structures involving hydrogen bonds with the amide group being formed as in (XI),



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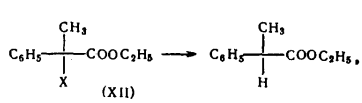
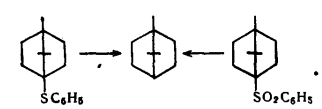


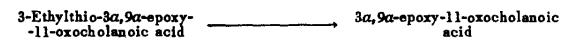
(XII)

where X = SC_6H_5, SOC_6H_5, or $SO_2C_6H_5$, is probably incorrect, since the same results (racemisation of the sulphide and reversal of the configuration of the sulphone) are also obtained when the amide group is replaced by an ester group as in compound (XII). In the latter case[16] the degree of racemisation was somewhat greater (25% for *p*-tolylsulphonylpropionate) but the configurational relations remained the same as before. This indicates mainly the specificity of the stereochemical mechanism of the hydrogenolysis and not a peculiarity in the structure of the substrate molecule although in some cases the effect of structure may be significant.

The fact that the hydrogenolysis of ethylthio- and phenylthio-phenylpropionate results in the formation of slightly optically active α-phenylpropionic acid (0.24 and 0.35% of the optical activity[16]) shows that an associative mechanism operates at the same time as the main, dissociative mechanism. A rigid structure, excluding the possibility of the reversal of configuration, favours a process involving the retention of configuration. Thus the desulphuration on nickel of both 4-bornyl phenyl sulphone and phenylthiobornane results in the formation of bornane[17]:



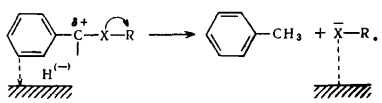
The desulphuration of compounds (XIII) on nickel gives 3α,9α-epoxy-11-oxocholanoic acid (XIV) ($[\alpha]_D$ = 88.1°), also with retention of the configuration by virtue of the rigid structure[18]:



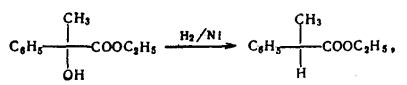
3-Ethylthio-3α,9α-epoxy--11-oxocholanoic acid (XIII) → 3α,9α-epoxy-11-oxocholanoic acid (XIV)

If one bears in mind that the behaviour in the last cases described is determined by the presence of a rigid molecular skeleton and they can scarcely be considered together with the hydrogenolysis of sulphur-containing propionates, the most rational explanation of the very great difference in the behaviour of sulphides and sulphones must be that provided by Bonner's mechanism, according

to which the adsorption of a sulphone molecule on the surface occurs via an oxygen atom, this being followed by the reaction of the hydrogen already adsorbed on the surface with the substrate molecule. The details of this process are as follows. It may be expected that in the hydrogenolysis of benzyl compounds of the type $C_6H_5CH_2-X-R$ adsorption on nickel will result in the transfer of the ring π electrons to the catalyst, as a result of which the α-carbon atom will acquire a certain positive charge which will facilitate attack by a hydride ion formed on the catalyst surface by dissociation of the H_2 molecule into H^+ and H^-. The reaction proceeds with reversal of configuration by an associative mechanism:



Thus if the molecule contains strongly chemisorbed groups which enhance the electron-donor properties of the catalyst, then, as for sulphones, the rupture of the C–S bond does in fact result in inversion of configuration. The validity of this mechanism and the effect of chemisorption have been confirmed by the study of hydrogenolysis of atrolactic acid and its *O*-derivatives. Indeed under the conditions of the hydrogenolysis of sulphides methyl and ethyl L-(+)-atrolacetates gave methyl and ethyl L-(-)-2-phenylpropionate:



with a low degree of racemisation[10,11] (Table 2).

TABLE 2. Hydrogenolysis of optically active derivatives of 2-phenylpropionic acid on nickel and palladium catalysts.

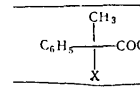
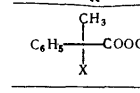
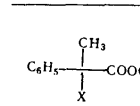
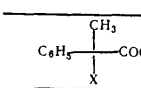
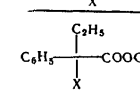
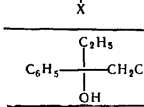
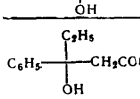
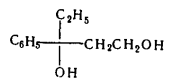
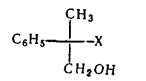
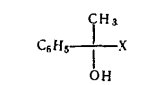
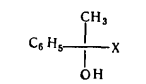
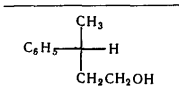
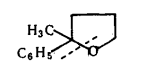
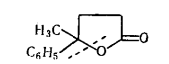
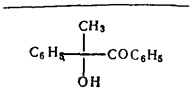
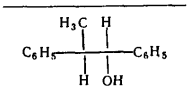
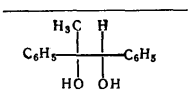
Initial compound			Catalyst, time and temperature of reaction	Product		Change in configuration	Type of mechanism	Refs.
structure	X	configuration, $[\alpha]_D$		$[\alpha]_D$	optical activity, %			
1	2	3	4	5	6	7	8	9
	OH	*D* −5.0 *L* +5.0	Ni, 4 h	*D* +86		no change	S_Ni	19
	OH	*D* −20 *L* +26.1 *L* +25.3	Ni, 3 h Ni, 3 h Ni, 17 h Ni, 37 h	*D* +45.5 *L* −35.7 *L* −25.0 *L* −73.2	79 73 66	no change ditto » »	» » » »	19 19 19 26
	OCH_3	*D* +46.2 *D* +47.9	Ni, 2 h	*D* +53.0 *D* +53.7	72 83	» »	» »	30 31
	OC_2H_5	*L* −31.9		*L* −53.4	90	»	»	31
	$OCH_2C_6H_5$	*L* −10.9		*L* −51.9	87	»	»	31
	OC_3H_7		do not react					31
	OC_4H_9							31
	OC_6H_5	*D* +6.2			95	inv.	S_N2	31
		L −2.1		*D* +30.5	95.3	»	»	26
		D +1.2	Ni, 8 h	*L* −6.1	93	»	—	26
		D +6.2	5% Pd/C		47	no change	S_Ni	31
	$OC_6H_4CH_3$-*o*	*D* −7.25	Ni	*L* −31.2	96	inv.	S_N2	24,32
			5% Pd/C		48	no change	S_Ni	24,32
	$OC_6H_4CH_3$-*p*	*L* +3.50	Ni	*D* +23.3	92	inv.	S_N2	24,32
			5% Pd/C		52	no change	S_Ni	24,32
	$OC_6H_4OCH_3$	*L* +13.6	Ni	*D* +34.2	95	inv.	S_N2	24,32
			5% Pd/C		49	»	»	24,32
	$OC_6H_4OCH_3$	*D* −8.4	Ni	*L* −28.2	94	»	»	24,32
			5% Pd/C		64	»	»	24,32
		D +4.81	Ni	*L* −29.6	91	»	»	24,32
	$OCOCH_3$	*L* −26.3	Ni	*D* +43.2	67	»	S_N2	33
	$OCOC_2H_5$	*D* +33.3	Ni	*L* −54.9	82	»	S_N2	33
	$OCOC_6H_5$	*L* −33.6	Ni	*D* +23.9	34	»	S_N2+S_N1	33
	NH_3^+	+5.48	Ni, 5 h	+8.57				30
	NHOOCH		do not react					30
	Cl	*L* +2.36	7.7% Pd/C	*L* −7.2	18.1	no change + rac.	S_Ni+S_N1	26
	Cl	*D* −2.01	Ni	0		rac.	S_N1	26
		D −21.3	Pd/C	*D* +9.14		no change	S_Ni	35
		L +20.2	Pd/C	*L* −7.0		ditto	S_Ni	35
	OH	+24.0	Ni, 60°		83	»	S_Ni	29
			Ni, 15°		94	»	»	29
	$OCOC_6H_5$	+28.7	Ni, 15°		10	inv.+ rac.	S_N2+S_N1	29
		+13.3	Ni	−14.5	45	no change	S_Ni	27
		+19.6	Pd/C	+10.7	60	inv.	S_N2	27
		+2.44	Ni	−20.8	100	no change	S_Ni	27
		2.68	Cu	−15.8	69	ditto		27
		2.68	Co	−17.5	76	»		27
		2.44	Pd/C	+14.4	70	inv.	S_N2	27
		2.68	Pd	+13.0	54	»	»	27

TABLE 2 (contd.)

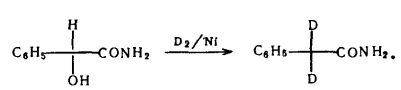
Initial compound: structure	Initial compound: X	Initial compound: configuration, $[\alpha]_D$	Catalyst, time and temperature of reaction	Product: $[\alpha]_D$	Product: optical activity, %	Change in configuration	Type of mechanism	Refs.
1	2	3	4	5	6	7	8	9
		−49.5	Ni	−14.5	98	no change	S_Ni	27
		−46.0	Cu	−13.0	100	ditto	»	27
		−38.7	Co	−10.0	92	»	»	27
		−49.5	Pd/C	12.2	88	inv.	S_N2	27
		−47.6	Pd	8.78	66	»	»	27
	C_2H_5	−5.95	Ni, 0.75 h	9.72		no change	S_Ni	38
	OC_6H_5	−15.0	Ni	8.4	70	inv.	S_N2	46
			Pd	10.0	84	»	»	46
	$OC_6H_4CH_3$-*p*	−48.2	Ni	13.2	92	»	»	46
			5% Pd/C	13.0	90	»	S_N2	46
	$OC_6H_4CH_3$-*o*	+12.1	Ni	−10.9	87	»	»	46
			5% Pd/C	−9.3	74	»	»	46
	$OC_6H_4OCH_3$-*p*	+52.8	Ni	−11.0	87	»	»	46
			5% Pd/C	−10.7	85	»	»	46
	C_2H_5	+17.4	Ni; 1.5 h	+9.72	42	no change	S_Ni	40
					64	ditto	S_Ni	41
	CH_2COOCH_3	+9.43	Ni	−33.5	94	»	»	27
			5% Pd/C	+36.9	100	inv.	S_N2	27
	$CH_2CH_2COOCH_3$	+29.9	Ni	+22.6	96	no change	S_Ni	27
		−30.8	10% Pd/C	+21.2	91	inv.	S_N2	27
	CH_2CH_2COOH	+22.5	5% Pd/C	−16.0	84	»	»	27
		+5.8	Ni	+23.6	100	no change	S_Ni	28,49
			5% Pd/C	+22.1	93.6	ditto	»	28,49
	CH_2CH_2OH	−61.4	Ni	−30.8	74	»	»	27
		−66.5	5% Pd/C	+40.9	91	inv.	S_N2	27
	$CH_2CH_2CH_2OH$	−7.44	Ni	−15.4	95	no change	S_Ni	27
			5% Pd/C	+14.7	91	inv.	S_N2	27
		−5.95	Ni; 0.75 h	+10.94		no change	S_Ni	36
		+3.40	Ni	−12.6	82	ditto	S_Ni	36
			5% Pd/C	+10.7	70	inv.	S_N2	36
		−61.9	1—5% Pd/C	2.35	10	rac.	S_N1	28
			Pd/C	−59.5				47
			$Cu—Cr_2O_3$	+63.5				47
			$Cu—Cr_2O_3$ 200°, 100 atm	11.8				47

* The ring is hydrogenated.

** Foraminate palladium was used.

A product with rotation of the opposite sign was obtained when L-(-)-atrolactate was used as the starting material. Consequently hydrogenolysis occurs with retention of the configuration. Thus the hydrogenolysis of C–SR and C–SOR bonds involves racemisation, the hydrogenolysis of $C–SO_2R$ occurs with retention of the optical activity and reversal of the configuration, while the hydrogenolysis of C–OH bonds occurs with retention of both the optical activity and configuration, which confirms Bonner's mechanism [19]. This mechanism is also confirmed by studies of isotope exchange in the hydrogenolysis of optically active compounds [20].

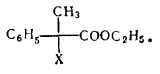
When a deuteriated Raney nickel catalyst in deuteriomethanol acts on L-(+)-mandelamide, dideuteriophenylacetamide is formed [21]:



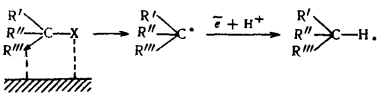
In this process up to 1.7 atoms of deuterium per molecule enter into the benzene ring, which is regarded as proof that the ring is adsorbed on the catalyst surface. Under the same conditions the exchange in (+)-2-phenylpropionamide occurs at the α-C atom and in CH_3 and C_6H_5 groups.

The rate of exchange exceeds initially the rate of racemisation but after 8.5 h the two rates differ only slightly[22]. Identical rates of isotope exchange and racemisation are characteristic of an associative mechanism[23]. These data confirm that, when the substrate contains molecules strongly adsorbed on the catalyst surface and behaving as a catalyst poison (thioethers, sulphoxides), the hydrogenolysis products are fully racemic, but when the molecules contain substituents which do not give rise to appreciable hindrance of the catalytic process and can be adsorbed reversibility, Walden inversion of configuration takes place with almost complete retention of the optical activity, and in some cases the initial configuration is also retained (in atrolactate). These observations led Bonner and then Mitsui, Imaizumi, and others to formulate a hydrogenolysis mechanism based on the hypothesis of nucelophilic substitution at the catalyst surface[24].

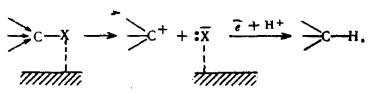
Several reviews exist, mainly in Japanese, but these are very incomplete[7,25] and it is therefore desirable to summarise studies in this field, considering them from the point of view of the study of the nature of the active surface. The following possible reaction mechanisms are examined below, using the hydrogenolysis on nickel of a 2-phenylpropionate or similar compounds as example:



1. Radical splitting is observed for sulphur-containing compounds (X = SC_6H_5, SOC_6H_5); these are powerful poisons of the nickel catalyst on which the SR group is strongly adsorbed; one of the substituents behaves as an electron acceptor, while the adsorption of C_6H_5 and $COOC_2H_5$ groups is much weaker. The C–S bond splits, a proton and an electron adding to the resulting radical and forming a racemic product:



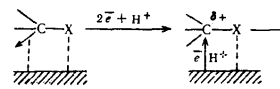
2. An S_N1 mechanism is possible when one or several substituents are weakly chemisorbed and behave as electron donors; The C–X bond (X = SC_6H_5, SOC_6H_5) splits with the formation of a carbonium ion, the addition of hydrogen to which is non-stereospecific and results in the formation of a racemic product:



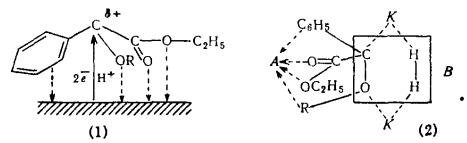
When the carbonium ion is unstable, the addition of $H^+ + 2e$ occurs before the removal of X and the product may contain an admixture of an active compound with inverted initial configuration. Steric hindrance favours the occurrence of the S_N1 mechanism.

3. An S_Ni mechanism is possible when adsorption of X (X = OH, OAlk) is weak and insufficient for the rupture of the C–X bond, and in the absence of appreciable steric hindrance involving the C_6H_5, $COOC_2H_5$, and OR groups. It is assumed that a kind of a cyclic compound is formed from the reacting molecule and the catalyst surface.

The presence of the donor benzyl group results in the attraction of electrons to the catalyst surface which causes the α-carbon atom to acquire a certain positive charge; electrons and protons pass from the catalyst to this atom with the formation of a product with initial configuration:



Mitsui[24], who considered the details of the geometry of the transition state, suggests that the adsorption of all the groups (C_6H_5, $COOC_2H_5$, and OR) occurs on the same area of the catalyst surface [scheme (1)]. In terms of the multiplet theory, this scheme may be represented by formula (2):



(1) (2)

In this scheme the centres A and B cannot be identified with the K' centres which are postulated in the multiplet theory to satisfy the principle of micro-reversibility[6].

4. The reaction has an S_N2 mechanism when there is steric hindrance to adsorption of the groups at the asymmetric carbon atom (the hindrance may occur on the catalyst side — when inhomogeneous and geometrically or energetically distinct centres are present on the catalyst surface). For example, in phenoxypropionates (X = OC_6H_5) this group [the CH_3 group? (Ed. of Translation)] cannot be adsorbed alongside the C_6H_5 and $COOC_2H_5$ groups on the same surface, as in the S_Ni mechanism, and they are in fact adsorbed on different areas of the surface, which lowers the steric hindrance to adsorption. Mitsui[24] assumes that, for adsorption of this type to occur, the molecule must be adsorbed on sterically opposite regions of the surface, for example on different sides of the surface of narrow pores.

The multiplet mechanism makes it possible to represent this type of disposition of "extra-indicial"† substituents at the asymmetric carbon atom by assuming the adsorption of the phenyl group in C_6H_5O at the centre A and of the methyl and ethoxycarbonyl groups at a second centre (B). The hydrogenolysis of the C–O bond for this type of disposition of the "extra-indicial" groups results in inversion of configuration (see the mechanism on p. 552).

The suggested mechanism of catalytic hydrogenolysis is based on the study of the hydrogenolysis of a large number of compounds of different structures, mainly derivatives of atrolactic acid and compounds containing the benzyl group with the substituents R′ and R″:

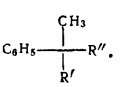


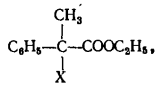
Table 2 lists all the known (up to 1965 inclusive) examples of the hydrogenolysis of such optically active compounds, whose number is steadily increasing. The

† A group of atoms on the catalyst surface which fits the configuration of the reacting group of the adsorbed molecule is known as the "index" in multiplet theory (Ed. of Translation).

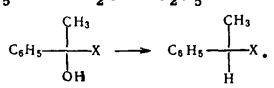
hydrogenolysis of C–O, C–N, C–Cl, and C–C bonds on Raney nickel and palladium catalysts has now been investigated.

Hydrogenolysis of the C–O Bond

The hydrogenolysis of compounds with the general formula



has been studied. The hydrogenolysis of methyl and ethyl atrolactates on nickel occurs stereospecifically by an S_Ni mechanism with retention of the initial configuration[19,26]. The effect on the hydrogenolysis of increasing distance between the $COOC_2H_5$ group and the asymmetric carbon atom has been examined in compounds with X = $= CH_2CH_2COOC_2H_5$ and $CH_2COOC_2H_5$:

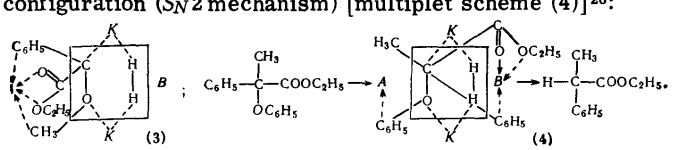


In these compounds, as in the atrolactates[19], the initial configuration is retained, a higher percentage of optical activity being preserved (up to 100% for X = CH_2CH_2. $.COOC_2H_5$[27,28]). However, on palladium/charcoal catalysts these compounds behave differently: the configuration of esters is inverted, while that of the acid (X = $= CH_2CH_2COOH$) is retained, as with the nickel catalyst[28].

If the carboxy group is close to the asymmetric carbon atom, as for example in ethyl 2-hydroxy-2-phenylbutyrate and its benzoyl derivative[29], the hydrogenolysis of the ester on nickel in the presence of added alkali takes place with retention of the configuration and the optical activity (up to 94%), the lowering of reaction temperature favouring greater stereospecificity (S_Ni mechanism). In the benzoyl derivative the optical activity is retained only to the extent of 10%, which is evidence of S_N2 and S_N1 mechanisms, predominantly the latter. This also indicates that the approach of the asymmetric carbon atom to the catalyst surface favours a change to an ionic reaction mechanism involving extensive racemisation of the product.

Alkoxypropionates. The hydrogenolysis of this group of compounds has been studied using nickel and palladium catalysts. On nickel methoxy- and ethoxy-propionates (X = OCH_3 and OC_2H_5) yield 2-phenylpropionate of high optical purity (72–90%) with retention of the initial configuration [multiplet scheme (3)][30,31].

Greater structural complexity of a substituent has differing effects on the reaction. Thus introduction of the benzyloxy-group (X = $OCH_2C_6H_5$) does not influence the stereospecificity of adsorption and the retention of the optical activity (up to 87%), while introduction of propyloxy- or butyloxy-groups (X = OC_3H_7 and OC_4H_9) prevents hydrogenolysis altogether, as a result of high steric hindrance and weak adsorption. An increase in the extent of adsorption of the substituent, for example when a phenoxy--group (X = OC_6H_5) is introduced, favours hydrogenolysis with retention of optical activity (93–95%) and inversion of configuration (S_N2 mechanism) [multiplet scheme (4)][26]:



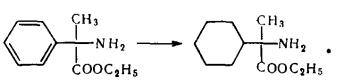
Inversion of configuration with retention of much of the optical activity (88–95%) is also observed for *o*- and *p*-cresyloxy- (X = $OC_6H_4CH_3$), *o*- and *p*-anisyloxy- (X = $= OC_6H_4OCH_3$), and β-naphthyloxy-propionates (X = $= OC_{10}H_7$).[32]

The hydrogeneolysis on 5% palladium/charcoal takes place in a different manner. Phenoxy- and *o*- and *p*-cresyloxy-propionates react by an S_Ni mechanism with retention of configuration (albeit with low specificity – 47, 48, and 52% respectively) which indicates that an S_N2 mechanism makes a certain contribution. However, *o*- and *p*-anisyloxypropionates undergo hydrogenolysis on palladium/charcoal by an S_N2 mechanism with reversal of configuration, the relatively low optical activity (49 and 64%) of the product indicating a greater contribution of the S_N1 mechanism[24,32].

Acyloxypropionates (X = OCOR). Whereas the hydrogenolysis of methoxy- and ethoxy-propionates on nickel occurs with retention of configuration, the hydrogenolysis of aceotoxy- and propionyloxy-propionates on nickel proceeds by an S_N2 mechanism with inversion of configuration and fairly high stereospecificity (67 and 82% of optical activity retained). On the other hand, the benzoyloxy-derivatives also undergo the inversion of configuration (S_N2 mechanism) but in addition there is a marked decrease in the optical activity of the product (optical purity 34%), which suggests the simultaneous occurrence of the S_N1 mechanism as a result of strong adsorption of the benzoyloxy-group[33].

Attempts at Hydrogenolysis of the C–N Bond.

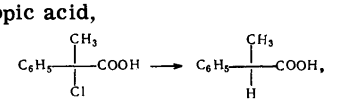
The replacement of the oxygen atom in the atrolactate molecule by nitrogen may result in a change of the mode of reaction. Thus methyl (+)-formamido-2-phenylpropionate is not hydrogenated on Raney nickel, while in ethyl (+)-2--amino-2-phenylpropionate the benzene ring is hydrogenated with the formation of ethyl (+)-2-amino-2-cyclohexyl-propionate[30]:



Probably the free amino-group facilitates the hydrogenation of the ring[34]. It is striking that this reaction takes place only under hydrogenolysis conditions: on platinum at 4 atm (25°) the ring is not hydrogenated. However, recently[33] it has been shown that at 150° and 60 atm the hydrogenolysis of the C–N bond in 2-amino-2-phenyl-propionic acid occurs on palladium/charcoal with retention of configuration and 70% of the optical activity.

Hydrogenolysis of the C–Cl Bond (X = Cl)

The hydrogenolysis of the C–Cl bond in L-(+)- and D-(-)-2-chloro-2-phenylpropionic acid on 7.7% palladium/charcoal catalyst with formation of L-(-)- and D-(+)-hydratropic acid,

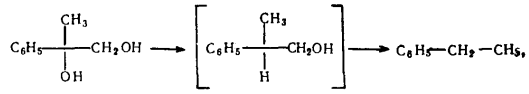


was the first example of hydrogenolysis of an optically active benzyl derivative[35]. The reaction takes place by an S_Ni mechanism with retention of configuration (the

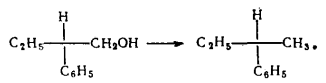
statement in Ref. 35 that the configuration changes is erroneous, see Bonner and coworkers[19]). When the hydrogenolysis is carried out on nickel at a higher temperature, the product is partially or completely racemised, i.e. the reaction takes place to a considerable extent by an S_N1 mechanism[26].

Hydrogenolysis of the C–O and C–C Bonds in Alcohols and Glycols

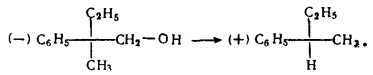
The reduction of the ester group in atrolactates yields a number of corresponding optically active glycols whose hydrogenolysis takes place both at C–O and C–C bonds, for example with formation of ethylbenzene from 2-phenylpropanediol by the following mechanism:



probably via the intermediate formation of phenylpropanol. This pathway is indicated by the hydrogenolysis of 2-phenylbutan-1-ol, for example, which takes place with retention of the configuration of 2-phenylbutane[36]:

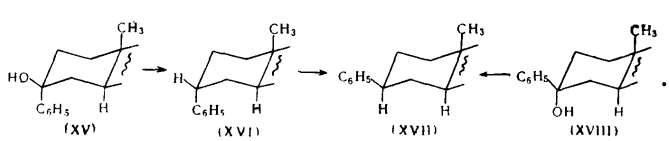


In the hydrogenolysis of phenylpropanediol carbon monoxide is formed from the C_1 atom as a result of the rupture of the C–C bond, which has been demonstrated by the hydrogenolysis of labelled [1-^{14}C]2-phenylpropane-1,2-diol.[37] Reaction by this mechanism should take place largely with retention of configuration, and this has been confirmed by the hydrogenolysis of (-)-2-methyl-2-phenylbutanol on nickel to (+)-2-phenylbutane[21], with retention of 70% of optical activity:



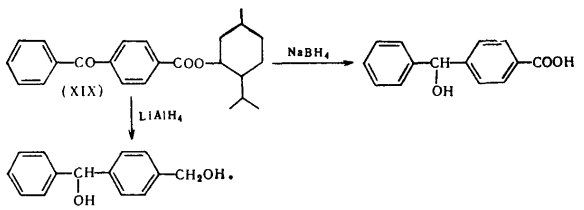
(Bonner[38] erroneously put forward an S_N2 mechanism; actually there is no inversion of configuration and the reaction has an S_Ni mechanism[39].) The hydrogenolysis of (-)-2-phenylbutan-2-ol also occurs with retention of configuration and leads to (-)-2-phenylbutane, 42% of optical activity being preserved[40,41].

These data show that the presence of two strongly adsorbed groups, phenyl and hydroxyl, favours the retention of the initial configuration in hydrogenolysis on nickel. The structure of that part of the molecule which is not adsorbed has little effect on the reaction mechanism. Thus the hydrogenolysis on nickel of the OH group in 3α-phenylcholestan-3β-ol (XV) proceeds with high stereospecificity and retention of configuration, 3α-phenylcholestane (XVI)[42] being formed, which is then slowly converted into 3β-phenylcholestane (XVII). The latter is readily obtained by the hydrogenolysis of 3β-phenylcholestan-3α-one (XVIII):

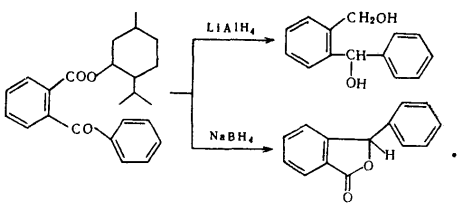


In the hydrogenolysis of 2-phenylethanol the introduction of substituents at the C_2 atom has a significant effect on the proportions of C_1–C_2 and C–O bonds hydrogenolysed, whereas the introduction into the *para*-position of electron-donor or electron-acceptor groups does not affect these proportions[39,43]. The absence of the latter effect indicates only a weak electron interaction and only a weak steric effect of these groups on the stereospecific adsorption of the asymmetric atom participating in the hydrogenolysis.

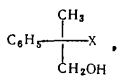
Indeed the steric effect of the asymmetric group is not "transmitted" via the benzene ring when attempts are made to achieve asymmetric synthesis. Thus in the reduction of *p*-benzoylbenzoate by $LiAlH_4$ or $NaBH_4$ inactive products are formed[44]. The action of CH_3MgI on the keto-group in compound (XIX) (asymmetric McKenzie synthesis) also leads to an optically inactive product:



The same result was obtained[45] in the reduction of the corresponding *ortho*-substituted menthyl ester:

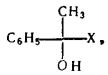


The study of the hydrogenolysis of the hydroxy-ethers of the general formula



where X = OC_6H_5, $OC_6H_4CH_3$, $OC_6H_4OCH_3$-*o*, and $OC_6H_4OCH_3$-*p*, showed that these substances undergo reversal of configuration both on nickel and on 5% palladium/charcoal but retain a high percentage (up to 84–92%) of their optical activity. This finding differs from the results obtained with phenylpropionates of the corresponding structure (replacement of CH_2OH by $COOC_2H_5$) whose initial configuration was retained on hydrogenation on palladium[46].

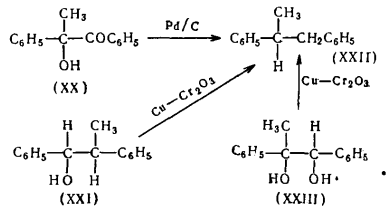
When the distance of the CH_2OH group from the asymmetric centre in the molecule is increased, the configuration is inverted on palladium/charcoal and preserved on nickel. The compound tested had the formula



where X= CH_2CH_2OH and $CH_2CH_2CH_2OH$.

Hydrogenolysis on other catalysts has been little studied. Barnes and Juliano[47] showed that in the hydrogenation of compounds (XX) on palladium/charcoal at a low temperature and of compound (XXI) on a Cu–Cr_2O_3 catalyst at 200°

and 100 atm the optically active 1,2-diphenylpropane (XXII) is formed, with retention of configuration:



However, the formation of L-(+)-(XXII) in the hydrogenolysis of L-(-)-(XXIII) involves extensive racemisation (81.9%).

Comparison of the Stereospecificity of Nickel and Palladium Catalysts in Hydrogenolysis

The study of the hydrogenolysis of optically active compounds permits a more profound understanding of the interaction between the reacting molecule and the catalyst surface. The differences in the mechanisms of hydrogenolysis may be due, on the one hand, to the structure of the reacting molecule, and, on the other hand, to the nature of the catalyst surface. The occurrence of S_Ni and S_N2 mechanisms on various catalysts is interpreted[24] as a result of the adsorption of various groups of the reacting molecules on "different sites" on the catalyst surface or on the opposite sides of the narrow pores in the surface where the adsorption of different sterically hindered groups of the molecule is facilitated, which in fact results in the inversion of configuration. Accordingly, it is to be expected that finely porous catalysts with a larger surface area will tend to give rise to reactions by an S_N2 mechanism, while catalysts with a more homogenous surface, without projecting centres, will give rise to reactions by an S_Ni mechanism.

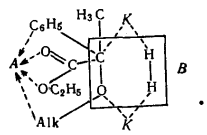
This difference may serve as experimental proof of the presence of projecting centres on the catalyst surface, which are active in relation to the adsorption of particular groups in the molecule; this can serve as an additional technique in the attempts to study the surface of a catalyst by catalytic reactions involving complex molecules which do not undergo inversion of configuration during the reaction[1].

A number of striking features in the behaviour of nickel and palladium has already been noted in the examination of the hydrogenolysis of compounds of different structures. Let us consider these findings in greater detail. Table 2 summarises all the experimental data on hydrogenolysis on nickel and palladium catalysts.

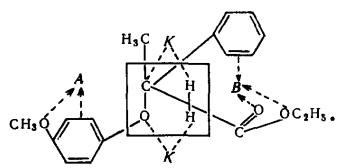
The hydrogenolysis of ethyl 2-phenoxy-2-phenylpropionate (X = OC_6H_5) and also the *o*- and *p*-cresyloxy- and *p*-anisyloxy-derivatives (X = *o*- and *p*-$OC_6H_4CH_3$ and *p*-$OC_6H_4OCH_3$) takes place on nickel by an S_N2 mechanism with inversion of configuration (Table 2). This presupposes the adsorption of aryloxy- and other groups on sterically different surfaces as a result of steric hindrance to adsorption on a single area of the surface. The hydrogenolysis of alkoxy-compounds, for which steric hindrance is less, can also occur on a single area of the surface, which involves no inversion of configuration, the reaction having an S_Ni mechanism. According to Mitsui and Imaizumi[24], "the Raney nickel catalyst has a surface structure such that aryloxypropionates are readily adsorbed on different areas of the surface". ‡ It is suggested that nickel has this type of structure, suitable for the adsorption of molecules whose reaction is sterically hindered because it contains many pores formed as a result of the leaching of the alloy[24]. However, the finding that foraminate palladium in no way differs from metallic palladium is evidence against this[46].

Palladium catalysts on carriers behave differently. Here the effect of the degree of coverage of the carrier surface by the metal on the mechanism of hydrogenolysis is observed. There are no data on the hydrogenolysis of alkoxypropionates and the reaction of phenoxypropionates on 5% palladium/charcoal proceeds, in contrast to the reaction on nickel, with retention of configuration (but it is less stereospecific, 47–52% of the optical activity being retained). When the substrate : catalyst ratio is changed from 1.4 : 0.1 to 1.4 : 15, the percentage of the optical activity retained is almost unaffected (it changes from 30 to 47%). However, the hydrogenolysis of *o*- and *p*-anisyloxypropionates on 5% palladium/charcoal takes place with inversion of configuration[24,26,32] (Table 2).

These data show that the product obtained on nickel retains its initial configuration when fairly strong adsorption of the alkoxy-group in the *A* centre takes place:



Starting with X = OC_6H_5, steric hindrance prevents the location of all three groups at the *A* centre and therefore the phenyl and carboxy-groups are adsorbed at the *B* centre, since OC_6H_5 is held in addition by the "index" centre *K*.



In view of the strong adsorption of oxygen on nickel, such displacement of the phenyl and carboxy-groups from the *A* centre occurs even in the presence of the phenoxy--group whereas on palladium/charcoal this happens only after the introduction of a second oxygen atom — in the anisyloxy-derivative (X = $OC_6H_4OCH_3$).

An increase in the palladium content above 10% alters the type of the mechanism (S_Ni) of the hydrogenolysis of phenoxypropionate[24] and leads to a product with inverted configuration, the reaction having an S_N2 mechanism. Furthermore, Table 3 shows that an increase in the palladium content from 1 to 10% sharply reduces the optical activity of the product (from 65 to 6%), but, starting with

‡ This quotation cannot be found in Ref. 24. Mitsui and Imaizumi[24] use an argument based on the simultaneous adsorption of a sterically hindered molecule on two opposing sides of a catalyst surface; this could occur in suitable pores in the catalyst (Ed. of Translation).

10% Pd, there is a gradual increase in the percentage of optical activity retained in the inverted product, up to 77% for 90% palladium/charcoal (Fig. 1, constructed on the basis of the data in Table 3, shows that the change in the mechanism of hydrogenolysis occurs when the palladium/charcoal catalyst contains 8% Pd). On pure palladium the percentage of the optical activity retained by the product is much lower.

Other Carriers

The deposition of palladium on barium sulphate instead of charcoal (5% Pd/$BaSO_4$) does not change either the reaction mechanism or the stereospecificity, compared with pure palladium (Table 3). However, comparison with the 5% palladium/charcoal catalyst shows that the mechanisms of the reactions on these catalyst are different: S_Ni for palladium/charcoal and S_N2 for palladium/barium sulphate.

According to Mitsui[24], the reason for this behaviour is that at a low palladium concentration the catalytic surface on which phenoxypropionate can be adsorbed is relatively small, since palladium is spread in a thin layer. As the thickness of the layer increases, which is achieved by increasing the concentration of palladium or reducing the surface area of the carrier (the use of barium sulphate),

TABLE 3. Effect of additives and the concentration of the catalyst on carriers on the mechanism of hydrogenolysis.

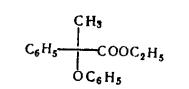
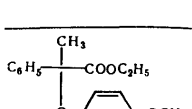
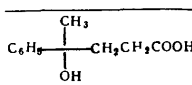
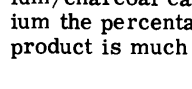
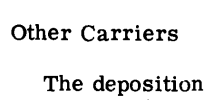
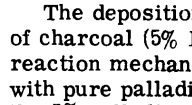
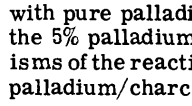
Initial compound: structure	Initial compound: configuration, $[\alpha]_D$	Initial compound: catalyst (% of metal on carrier)	Product: $[\alpha]_D$	Product: optical activity, %	Change in configuration	Type of mechanism	References
	*L*-(+)6.2	Pd/C 1%	*L* −20.3	65	no change	S_Ni	24
		10%	*D* +2.0	6	inv.	S_N2	24
		25%	*D* +5.9	18	»	»	24
		50%	*D* +9.5	30	»	»	24
		75%	*D* +15.6	49	»	»	24
		90%	*D* +24.8	77	»	»	24
		Pd	*D* +13.9	44	»	»	24
		Pd/$BaSO_4$ 5%	*D* +14.2	44	»	»	24
	D-(−)	Pd/Al_2O_3 0.2%	*D* +11.2	31	no change	S_Ni	24
		0.5%	*D* +5.2	15	ditto	»	24
		1%	*D* +1.1	3	»	»	24
		2%	*L* −5.9	16	inv.	S_N2	24
		5%	*L* −25.4	71	»	»	34
		10%	*L* −27.1	76	»	»	24
	D (−)9.5	Ni, 1 h	−28.4	70	»	S_N2	48
		Ni+0.5 g NaOH	−37.7	93	»	»	48
		0.5 g NaCl	−29.8	74	»	»	48
		0.5 g KBr	−33.9	84	»	»	48
	D (−)9.5	5% Pd/C	+13.3	33	no change	S_Ni	48
		Pd/C+0.001 mole NaOH	−34.1	85	inv.	S_N2	48
		Pd/C+0.001 mole HCl	−8.1	20	»	S_N2	48
		Pd/C+0.001 mole KBr	−26.4	65	»	S_N2	48
		Pd/C+0.001 mole NaCl	+11.2	28	no change	S_Ni	48
	L-(+)6.2	Ni/Kieselguhr	*D* +31.1	97	inv.	S_N2	24
		Ni(Urushibara catalyst)	*D* +32.1	100	»	»	24
	*L*(+)10.9	Pd/Al_2O_3 0.2%	*D* +29.5	81	»	S_N2	24
		1%	*D* +28.1	77	»	»	24
		5%	*D* +27.6	76	»	»	24
		Pd/C 1%	*D* +19.3	53	»	»	24
		5%	*D* +23.3	64	»	»	24
		50%	*D* +27.8	77	»	»	24
	+5.8	Pd/C 1%	+23.6	100	no change	S_Ni	49
		5%	+23.2	98.3	ditto	»	44

TABLE 3 (contd).

Initial compound: structure	Initial compound: configuration, $[\alpha]_D$	Initial compound: catalyst (% of metal on carrier)	Product: $[\alpha]_D$	Product: optical activity, %	Change in configuration	Type of mechanism	References
	−4.4	Pd/C 10%	−17.1	93.4	no change	S_Ni	49
		25%	−17.9	97.5	ditto	»	49
		50%	−17.7	96.6	»	»	49
		75%	−18.2	99.2	»	»	49
		Pd/C+HCl 5%	−16.7	91.1	»	»	49
	+1.88	Pd/C—(A) 1%	−20.9	84.5	»	S_Ni	49
		10%	−15.2	61.3	»	»	49
		50%	−8.2	33.2	»	S_Ni	49
	+1.38	Pd/C—(B) 1%	−9.9	54.6	»	S_N2	49
		10%	−8.8	48.1	»	»	49
		Pd/C—(A) 1% NaOH 10%	−12.5	68.6	»	»	49
			−8.7	47.4	»	»	49
	−14.9	Pd/C—(A) 1%	+15.7	84.5	inv.	S_N2	50
	+13.7	5%	−16.8	90	»	»	50
		20%	−19.5	95	»	»	50
	−14.9	Pd/C—(B) 10%	+18.7	91	»	»	50
	(+)33	Pd	−7.7	91	»	»	50
	(−)89	Pd/C 5%	+20.2	90.5	»	»	50
	56%	Pd/C—B 5%	−11.9	88	»	»	50
		Pd/C 10%	−14.1	95	»	»	50
	12.7%	Pd/R	−3.7	100	»	»	50
	56%	PtO_2 (+HCl)	−1.65	72	»	»	50
	+13.7°	Ni—R	+19.6	97	no change	S_Ni	
	−13.0°		−10.7	77	ditto	»	50
	12.7%		+13.6	65	»	»	50
	12.7%	Co—R	1.85	24	»	»	50
	(+)48	Pd/Ni	+12.0	5.5	»	»	50
	(+)48	Pt—Ni	11.7	6.5	»	»	50
	(−)65	Cu—Cr_2O_3	−18.3		»	»	50
	+48	Cu—R	+11.3	8	»	»	50
	−48	Co—R	−1.5	55.5	»	»	50
	−48	Pt/C	−8.1	80	»	»	50
	+34.4	Pd/C—(A) 1%	+13.6	85	inv.	S_N2	50
	−33.5	5%	−15.5	91	»	»	50
	+34.4	10%	+14.1	86.5	»	»	50
	−33.5	20%	−18.0	90	»	»	50
	+34.4	Pd/C—(B) 1%	+14.2	87	»	»	50
	−33.5	5%	−17.7	97	»	»	50
	+34.4	10%	+14.9	88.5	»	»	50
	−33.5	Ni	−13.3	85.5	»	»	50
	(+); 73%	Pt—C 5%	+18.0	94	»	»	50
	(+); 73%	Pd	+19.8	98	»	»	50

Note. The letter R denotes Raney catalysts.

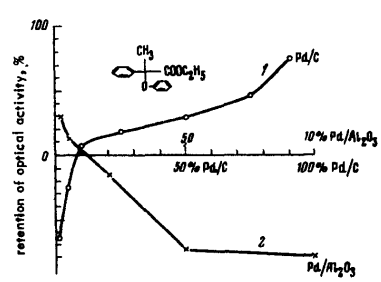


Fig. 1.

the microroughness of the surface becomes more pronounced and a substrate molecule can be adsorbed at two points on the surface, which leads to an inverted product. The stereospecificity of the reaction increases with the number of such centres, reaching a maximum (77% for Pd/C = = 9 : 1) and then falling sharply (44% for pure palladium).

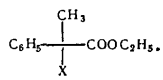
The explanation of this behaviour of pure palladium is[24] its lower dispersion and the absence of pores of suitable

dimensions. The behaviour of palladium/barium sulphate, whose specific surface and porosity are low, is also similar.

The replacement of charcoal by alumina leads to similar results, but here a change in the mechanism of hydrogenolysis is observed for 1.2 Pd/Al_2O_3 (Fig. 1, curve *2*). For this reason, the formation of structures favouring three-point adsorption on sterically different centres, which leads to inversion of configuration, begins on Pd/Al_2O_3 catalysts with a much lower palladium content. This type of behaviour of the Pd/Al_2O_3 catalysts may be due to the smaller specific surface of alumina compared with charcoal[24]. The change in mechanism on the palladium/charcoal and palladium/alumina catalysts is observed at the same degree of coverage of the carrier surface: about 3% of the monolayer. Hence it follows that for palladium dispersed into atoms on the surface the Pd–Pd distances between the centres are 13–15 Å, which corresponds to the dimensions of the phenyl(phenoxy)propionate molecule (Fig. 2). When the distances between the centres are reduced, conditions favouring an S_N2 mechanism are created. Regardless of the method of preparation, the nickel catalysts (Raney nickel, nickel on Kieselguhr, Urushibara nickel) probably have a surface structure such that the distances between the active centres do not exceed about 10 Å. On such centres the hydrogenolysis of phenoxypropionate takes place with inversion of configuration (Table 3).

The study of the effect of additives (NaOH, HCl, KBr) to the catalysts (nickel and palladium/charcoal) showed that, in the presence of alkali or potassium bromide (and to a lesser extent sodium chloride), the degree of inversion increases on both catalysts — on nickel catalysts there is an increase in the degree of inversion and on palladium catalysts a decrease in the percentage retention of the initial configuration: the contribution of the S_N2 mechanism increases. Addition of HCl to palladium/charcoal also increases the contribution of the S_N2 mechanism, but to a lesser degree than the addition of alkali and potassium bromide (Table 3)[48].

For other groups of the molecule, with different adsorption capacity and steric relations, a different type of variation with the catalyst concentration on the carrier and with the additive may be observed. Thus the hydrogenolysis of the sterically more complex molecule, ethyl 2-(*p*-anisyloxy)-2-phenylpropionate (X = $OC_6H_4OCH_3$),



on both nickel and palladium/charcoal and palladium/alumina catalysts involves the reversal of configuration over a wide range of palladium concentrations. The high degree of retention of the optical activity by the product also shows that here the structure of the substrate molecule determines the sterospecificity of the process. When the palladium content is increased from 0.2 to 50% on charcoal and alumina, there is little change in stereospecificity (53–81%)[24].

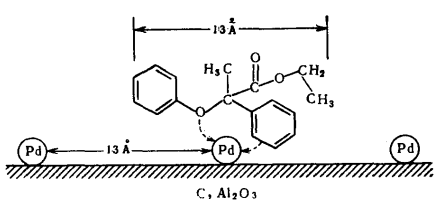
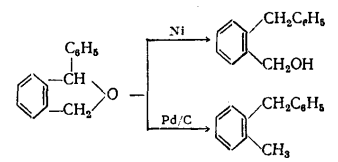


Fig. 2.

Hence it is evident that the difference between the nickel and palladium catalysts is also due to their different capacity to adsorb polar groups. In the case of phenoxypropionate steric factors predominate and the degree of coverage of the carrier surface by palladium greatly influences the reaction mechanism. In the hydrogenolysis of compounds with strongly adsorbed groups, for example the anisyloxy-group, the affinity of palladium for polar groups is the decisive factor; they become strongly adsorbed and the reaction proceeds with inversion of configuration, regardless of the palladium concentration on the carrier.

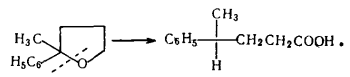
The much lower degree of adsorption on 7.7% palladium/charcoal compared with the nickel catalyst may be the reason for the partial retention (up to 18%) of the initial configuration (S_N2 + S_Ni mechanisms) in the hydrogenolysis of ethyl 2-chloro-2-phenylpropionate (Table 2)[26,35]. For example, the lower affinity of palladium, compared with nickel, for oxygen-containing groups explains also the different pathways of the hydrogenolysis of phenylphthalenes[48]; hydrogenolysis on nickel leads to *o*-benzoylbenzyl alcohol while on palladium/charcoal *o*-benzyltoluene is formed:



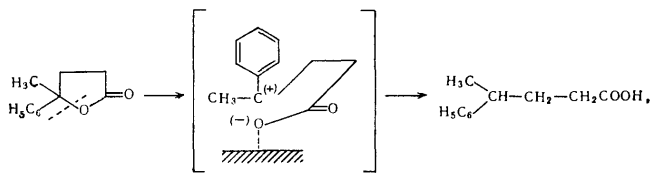
The presence in the reacting molecules of groups which can be strongly adsorbed has a significant effect on the reaction mechanism and it is interesting to compare the hydrogenolysis on nickel and palladium of a number of glycols and hydroxy-acids and their oxygen-containing derivatives. Thus the hydrogenolysis of atrolactic acid derivatives on nickel takes place mainly with the inversion of configuration, and the replacement of $COOC_2H_5$ by CH_2OH in these molecules does not alter the hydrogenolysis mechanism. However, the removal of the methoxycarbonyl group to a position more distant from the asymmetric centre by one or two CH_2 groups alters the mechanism to S_Ni on nickel, cobalt, and copper, probably because, as a result of an increase in the mobility of the alkyl chain, the molecule can be adsorbed without inversion of configuration on "one side" of the catalyst surface by way of "W-shaped" adsorption. In hydrogenolysis on palladium/charcoal catalysts the replacement of $COOC_2H_5$ by CH_2OH changes the S_Ni mechanism to the S_N2 mechanism, probably as a result of only weak chemisorption of the molecule on the surface. Here the removal of the $COOCH_3$ group further away from the asymmetric centre favours hydrogenolysis by an S_N2 mechanism[27]. However, if chemisorption is enhanced, for example by the replacement of methyl γ-hydroxy-γ-phenylvalerate (Table 2) by the free acid, then the reaction on both palladium and nickel proceeds by an S_Ni mechanism[28] and a change in the concentration of palladium does not alter the reaction mechanism and has little effect on the retention of optical activity (Table 3)[49]. The addition of HCl to the 5% palladium/charcoal catalyst is also without effect.

As pointed out above (see Table 2), benzoylated hydroxy-acids impede adsorption on nickel and change the mechanism from S_N2 to S_N1 [33]. There are no such data for hydrogenation on palladium. However, it is known that the hydrogenolysis of methyl γ-hydroxy-γ-phenylvalerate and butyrate involves the inversion of configuration [27] (Table 2), while the hydrogenolysis of the free acids proceeds by an S_Ni mechanism. In the hydrogenolysis of a benzoylated acid on palladium/charcoal catalyst in the presence of alkali a decrease in the degree of retention of the optical activity with increase in palladium content in the catalyst is observed, which indicates a gradual increase of the contribution of the S_N2 mechanism [49] (Table 3).

Different mechanisms are also observed in the hydrogenolysis of 2-methyl-2-phenyltetrahydrofuran (S_Ni on nickel and S_N2 on palladium/charcoal [27]).



However, when a second oxygen atom is present in the ring, for example in the hydrogenolysis of γ-phenylvalerolactone on palladium/charcoal,



the reaction proceeds by an S_N1 mechanism with extensive racemisation (10% of optical activity is retained) [28] (Table 2). The difference in the action of the catalysts can probably be accounted for by the lower affinity of palladium for electronegative elements [27].

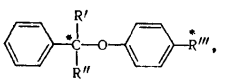
The stereospecificities of the nickel and palladium catalysts may be compared and the effect of the palladium concentration may be assessed by studying the hydrogenolysis of compounds capable of being adsorbed without much steric hindrance for any orientation on the catalyst surface. 2-Phenylbutan-2-ol was chosen as a model compound of this kind [50]. Tables 2 and 3 show that the hydrogenolysis of this alcohol and its methyl ether on foraminate (Raney) nickel, cobalt and copper catalysts and also nickel promoted with palladium and platinum proceeds with formation of 2-phenylbutane, retention of configuration, and high (up to 97%) stereospecificity [50]. It should be noted that in other studies [40,41] such high percentage retention of optical activity was not observed.

Palladium catalysts of different origins and with different palladium concentrations on charcoal as well as catalysts containing added acid (Pd/C–A) or base (Pd/C–B) also showed high stereospecificity, but the hydrogenolysis of 2-phenylbutan-2-ol and its methyl ether occurs with inversion of configuration (S_N2). Furthermore, whereas the hydrogenolysis of 2-phenylbutan-2-ol on the palladium/charcoal catalyst in alcohol occurs with inversion of configuration, in benzene the initial configuration is retained [50]. This demonstrates the different stereospecificities of the nickel and palladium/charcoal catalysts, which form intermediate complexes of different geometry because of the differences in the bond energies of the hydroxyl and the catalyst surface. The latter is significantly influenced by the solvent. In contrast to palladium/charcoal, the rate of hydrogenolysis on nickel is higher in polar oxygen-containing solvents.

However when significant steric hindrance prevents adsorption, as for example in the hydrogenolysis of 1-methyl-1-phenylpropyl hydrogen phthalate, then on Raney nickel promoted with platinum and palladium and also on palladium/charcoal, platinum/charcoal, and metallic palladium hydrogenolysis proceeds only by an S_N2 mechanism with inversion of configuration (Table 3) [50]. Thus the nature of the catalyst and the concentration of palladium on the carrier do not play any role in this case. Hydrogen adds, as it were, from "behind" the substituents adsorbed on the surface and hydrogenolysis proceeds with inversion of configuration.

Thus the study of the mechanism of the hydrogenolysis [51] of optically active compounds opens up new possibilities for the investigation of the active surface of catalysts and it is extremely interesting to investigate, apart from palladium/charcoal and palladium/alumina catalysts, also catalysts on other carriers with specific surfaces of the order of 10–100 $m^2\ g^{-1}$ in order to establish the lower limit of the concentration of palladium at which the mechanism of hydrogenolysis changes.

An increase in stereospecificity can probably also be obtained on dilute catalysts using specific carriers which adsorb selectively the optically active groups of the substrate molecule. This can be shown, for example, in the hydrogenolysis of diastereoisomers of the type:



(where $\overset{*}{R}'''$ contains the asymmetric centre) on a catalyst deposited on a carrier (natural or synthetic polymer, silica gel formed by a specific procedure [52–54], etc.) capable of asymmetric adsorption [55]. According to Kubitscheck and Bonner [44], in such a compound the asymmetric centres $\overset{*}{C}$ and $\overset{*}{R}'''$ do not interact sterically and consequently the reaction of the asymmetric carbon atom $\overset{*}{C}$ can serve as a kind of indicator of the stereospecificity of the process and $\overset{*}{R}'''$ determines the asymmetric adsorption.

Thus a change in the reaction mechanism can serve as an indicator of the stereospecificity of chemisorption during catalysis, which is sensitive both to steric and energy factors in the interaction between the groups of the substrate molecule and the catalyst surface. Thus for palladium/charcoal there is a limiting surface coverage equal to 3% of a monolayer, which results in a change of the mechanism (from S_Ni to S_N2) in the hydrogenolysis of phenyl phenoxypropionate.

Both pronounced sorption and strong steric interactions are observed on nickel. The adsorption is strong in the hydrogenolysis of chloropropionate (X = Cl, S_N1 mechanism). The adsorption is weaker in the hydrogenolysis of propionates with X = OH, OCH_3, C_2H_5, and $OCH_2C_6H_5$, alcohols, and glycols, and compounds with a long chain between the two adsorption points (S_Ni mechanism). Adsorption and steric hindrance occur in the hydrogenolysis of propionates when $X = OC_6H_4{-}OCOC_2H_5$, and of ethylene glycol monoethers (S_N2). Pronounced steric hindrance ($X = OCOC_6H_5$) leads to a mixed mechanism ($S_N2 + S_N1$).

Since strong adsorption and marked steric hindrance lead to a non-specific S_N1 mechanism, it is evident that the nickel surface exhibits considerable inhomogeneity, of both the geometrical and the energy type, i.e. a considerable degree of "microroughness", since an S_N1 mechanism

presupposes that the asymmetric carbon atom is distant from the catalyst surface.

Weak steric and adsorption interaction has been observed on the palladium/charcoal catalyst: (1) the weak adsorption of propionates with X = Cl, OC_6H_5, and $OC_6H_4CH_3$ leads to an S_Ni mechanism; (2) weak adsorption also gives rise to steric hindrance for the propionates with R = OC_6H_5 and OCH_3, alcohols, glycols, and compounds with long chains between the two points of weak adsorption (methyl esters of hydroxy-acids): an S_N2 mechanism obtains. However, enhanced adsorption (hydroxyvaleric acid) changes the mechanism to S_Ni (as on nickel).

Hence it may be concluded that the surface of the palladium/charcoal catalyst is geometrically and energetically more homogeneous than that of nickel and that polar groups are not strongly adsorbed on it. The reaction is always stereospecific: the asymmetric carbon atom is close to the surface and the reaction mechanism is largely S_Ni or S_N2. The steric hindrance associated with the "extraindicial" substituents in the multiplet reaction "index" can play a considerable role. Thus phenylpropionates with X = OC_3H_7 and OC_4H_9 do not react at all, while those with X = OC_2H_5 and $OCH_2C_6H_5$ undergo hydrogenolysis with retention of the original configuration. The bond energies Q_{OK} in the hydrogenolysis "index" must be corrected for the steric interaction between the OR radicals, in conformity with the principle of the energy correspondence of the multiplet theory of catalysis[56].

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REVERSIBLE VALENCE ISOMERISATION

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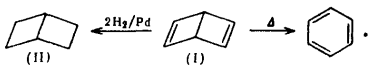
and I. A. D'yakonov

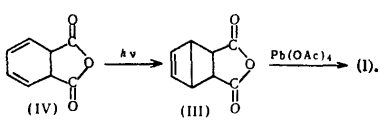
In recent years many examples of isomeric conversions have become known that differ phenomenologically from most ordinary isomerisations. A characteristic of the new type of isomerisation is that it occurs without displacement of atoms or atomic groups within the molecule. The isomerisations are accompanied by corresponding changes in the relative arrangement of σ- and π-bonds and only by small changes in interatomic distances and valence angles. In the literature, this kind of isomeric conversion has been given the name valence isomerisation [1]†.

A striking example of a valence-isomeric conversion is the recently described thermal isomerisation of "Dewar benzene", or bicyclo[2,2,0]hexa-2,5-diene (I) to ordinary benzene [5]:



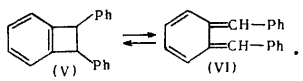
At room temperature "Dewar benzene" is fairly stable, having a half-life of 2 days, but at 90° it is converted into benzene in 30 min.

The structure of "Dewar benzene" was confirmed by examination of its nuclear magnetic resonance (NMR) spectrum and by its conversion on careful hydrogenation into bicyclo[2,2,0]hexane (II). The structure was also determined by synthesis: "Dewar benzene" was obtained by oxidising the anhydride of bicyclo[2,2,0]hex-2-ene-5,6-dicarboxylic acid (III) with lead tetra-acetate. It is of interest to note that the anhydride is formed by the photo-initiated valence-isomerisation of 1,2-dihydrophthalic anhydride (IV):



Valence isomerisations, like non-valence isomerisations, may be classified as reversible or irreversible. The isomerisation of the hydrocarbon (I) to benzene is an example of irreversible valence isomerisation. Isomerisations of this kind are very numerous (see reviews [2-4,6] and some original papers of recent years [7-37]).

Irreversible valence isomerisation occurs when two valence isomers differ greatly in their thermodynamic stability. When this difference is not great, dynamic equilibrium may be established between the valence isomers. This type of valence isomerism is termed reversible. An example that may be quoted is the recently described reversible valence isomerisation of *trans*-1,2-diphenylbenzocyclobutene (V) to *trans-trans*-5,6-dibenzylidenecyclohexadiene ($\alpha\alpha'$-diphenyl-*o*-quinodimethane) (VI) [38] (see also Freedman and coworkers [39]):



We shall give a number of other examples of this type of isomerisation below.

In recent years the term "valence tautomerism" has been increasingly used in publications outside the Soviet Union to describe the phenomenon of equilibrium valence isomerism. According to Rhodes [4], for the correct use of this term the following condition should be observed: "the corresponding isomers must be converted into each other under normal working conditions and the energy barrier to be overcome must be relatively small. If the latter condition is not fulfilled, it is better to call the compounds valence isomers".

The author does not say what is to be understood by normal working conditions. A study of the literature shows that other authors do not adhere to this kind of limitation in the definition of valence tautomerism. It is clear from papers we shall refer to later that valence-tautomeric conversions may include conversions that occur at widely different temperatures and pressures, and under widely different conditions of illumination, etc. The position of equilibrium between the valence tautomers can also have any value. As is pointed out below, at present systems are known in which equilibrium is largely displaced in the direction of one of the tautomers‡. Hence it follows that the energy barrier to be overcome when one tautomer is converted into another may vary appreciably from case to case.

Notwithstanding what has just been said, it must be recognised that the term "valence tautomerism" is not a good one. Firstly, although this term was proposed a long time ago, the concept of valence tautomerism itself was invested with a somewhat different meaning (see, for example, Ingold [40]).

The idea that valence tautomerism can occur was first put forward by Kekulé, who proposed a dynamic formula for the structure of benzene in 1872. [41] The term "valence tautomerism" itself was first used by Wieland in 1920–1922, who, like many other chemists of that time, regarded valence tautomerism as the rapid intramolecular oscillation of valence bonds [42,43]. Later, a meaning not differing substantially from the modern concept of resonance began to be applied to the concept of "valence tautomerism". As is known, the concept of resonance is based on the idea that the real state of a given molecule may be described by the superposition of several limiting structures, none of which occurs alone in the unexcited state. It is characteristic of the limiting structures that they have the same distances between corresponding atomic nuclei and the same angles between the atoms; they differ only in the arrangement of the π-electrons. Resonance structures do not have the significance of structural formula of real compounds and

† At present only three review articles on the subject of valence-isomeric conversions can be cited, and these have appeared in foreign journals [2-4]. These articles are, to a certain extent, already out-of-date, because many new experimental papers have been published since they appeared. No reviews of this kind have yet appeared in Soviet literature.

‡ In this connection it should be noted that a sharp line cannot be drawn between reversible and irreversible isomerisation. Processes that are now regarded as irreversible may in the future turn out to be reversible when new sources of energy are used or more sensitive methods of analysis are applied.

are only arbitrary constructs which may be used for molecular calculations by the method of valence diagrams. In contrast, valence tautomers, which are being considered here, are structures that really exist. Moreover, they differ from one another not only in the order of alternation of single and double bonds, as, for example, the oscillating benzene structures proposed by Kekulé and by Dewar, but also in the distances between atoms, in the valence angles, and in free energy content.

Secondly, the use of this term may give rise to the idea that the concept of valence tautomerism is related to, or even identical with, the concept of electronic tautomerism[44,45]. In fact both concepts differ in their content.

Notwithstanding what has been said above, the term "valence tautomerism" is now widely used in the literature. For this reason, and also because there is no other suitable name for this phenomenon, we are forced to retain this term in our review.

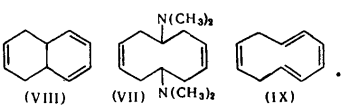
Since valence tautomerism is associated with reversible-valence-isomerisation phenomena, it should be possible to make a suitable change of terms and use the term "reversible valence isomerisation" instead of "valence tautomerism". To this, however, it must be objected that the new term is longer than the old one and therefore less convenient in use. The idea of tautomerism does not always fully correspond with the idea of reversible isomerisation. The difference lies in that in tautomerism a state of dynamic equilibrium is established, but this is not a necessary condition for reversible isomerisation. As confirmation of this we may cite as an example those reversible valence isomerisations (they are considered below) in which the direct reaction occurs under some conditions, for example, with ultraviolet irradiation, and the reverse reaction occurs under other conditions, for example, with heating. There is no state of equilibrium between valence isomers in such instances (and therefore these isomers cannot be regarded as valence tautomers), although this state could be achieved under certain conditions of irradiation and heating (and then a system of this kind should be regarded as tautomeric). Thus, the idea of reversible valence isomerisation embraces the idea of valence tautomerism, but the converse is not true. The question whether one term should be replaced by the other must therefore be answered in the negative.

The present review is devoted to a description of the phenomena of reversible valence isomerisation, which here also covers the field of valence tautomerism. Another no less interesting field, that of valence (intramolecular) rearrangements, is not considered. We might well have limited our remarks on valence rearrangements to this observation, if the error[4] was not frequently encountered that isomerisations can be called rearrangements and conversely. In this connection, it would be useful to consider what is meant by intramolecular rearrangement and how it differs from isomerisation.

In a number of available theoretical handbooks on organic chemistry a definition of the concept of rearrangement is either not given (see, for example, Ingold[46]) or the proposed definitions are not sufficiently rigorous and reliable[47,48]. Some authors[49-51], however, are agreed that the term molecular rearrangement should only be applied to a special group of reactions, be they substitutions, eliminations, or additions, in which the principle of minimal structural change is violated. Although this formulation of the concept of a new type of reaction must be considered somewhat vague (because of the vagueness of the principle itself), nevertheless at the present time it best meets the requirements of reality. On the other hand, it is quite clear that this definition is not applicable to the concept of isomerisation. Thus, it would be absurd to consider the question whether the principle of minimum structural change is preserved in isomerisation reactions. In these reactions only the structure changes, and not the composition, since only one molecule of final product is formed from one reacting molecule. In reactions of the intramolecular-rearrangement type a change always occurs not only in structure but also in composition, although in isolated instances the number of molecules reacting may be the same as the number of molecules formed.

The question of the mechanism of rearrangements requires special consideration. It is difficult to draw any conclusion on this point from the actual definition of these reactions (see above). However, there is now convincing published evidence (see p. 511 of the book by Temnikova[51]) that rearrangements may proceed in two ways, either by way of an active reaction complex (brought about by a so-called reaction with reaction-centre transfer), or by the rapid isomerisation in the course of the reaction of the initial compound or one of its intermediates. The fact that the reaction can proceed in the first way is a further argument against identifying rearrangements with isomerisations.

Everything that has been said here on reaction mechanism is also valid for valence rearrangements. It should be noted, however, that the experimental investigation of the mechanism of valence rearrangements presents great difficulties, because of the absence of appreciable displacement of the atomic nuclei in the conversion process. Only one example of valence rearrangement will be given here. The dioxide of the diamine (or the diquaternary ammonium salt) obtained from 1,6-bis(dimethylamino)-cyclodeca-3,8-diene (VII) undergoes thermal decomposition (120–150°) with the formation of *trans*-1,4,9,10-tetrahydronaphthalene (VIII). According to Grob and Schies[52], the latter is formed by valence isomerisation of the unstable tetraene (IX), a product of the normal cleavage of the diamine dioxide (VII) or quaternary salt. Since the intermediate tetraene (IX) has not been isolated, the proposed mechanism cannot be considered proved. It is possible that the tetrahydronaphthalene (VIII) is formed directly from the diamine dioxide (or the diquaternary ammonium salt), without an intermediate stage (see, however, Grob and coworkers[53]).

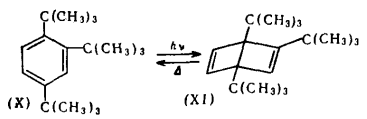


(VIII) (VII) (IX)

After the foregoing discussion on valence isomerisation (reversible and irreversible), valence tautomerism, and finally, molecular rearrangements including valence rearrangements, we may proceed to a more detailed examination of the phenomena of reversible valence isomerisation, which in fact is the main theme of the present paper.

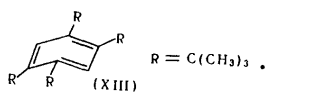
In recent years the valence-isomeric conversions of benzene and its homologues have attracted particular attention. It is curious to note that the structures of the valence isomers of benzene have a formal similarity to the benzene structures proposed in their time by Dewar and by Ladenburg (hence the names "Dewar benzene" and "Ladenburg benzene"). An example of the irreversible valence

isomerisation of "Dewar benzene" into ordinary benzene was given on p. 559 (see also Criegee and Zanker[54]). An example of reversible valence isomerisation of this kind is the conversion of 1,2,4-tri-t-butylbenzene (X) into 1,2,4-tri-t-butylbicyclo[2,2,0]hexa-2,5-diene (XI), which proceeds under the action of light[55]. The isomer (XI) can be separated from the remaining products of photoconversion by thin-layer chromatography and purified by distillation under high vacuum at room temperature. It has been proved that the hydrocarbon (XI) is monomeric; its structure has been confirmed by ultraviolet and NMR spectra. When heated to 200° for 15 min, it is converted into the initial tri-t-butylbenzene (X):



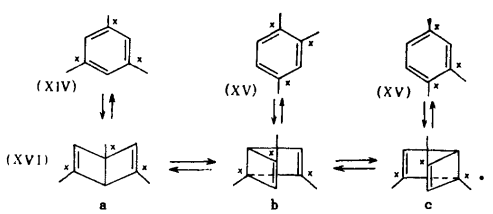
There is no dynamic equilibrium between the isomers, but it may be supposed that this equilibrium would be achieved under suitable conditions (illumination + heating).

In this instance the formation of the bicyclic isomer (XI) from tri-t-butylbenzene is promoted by the steric effect of the substituents. There are grounds for supposing that the carbon atoms in the 1,2,4-tri-t-butylbenzene ring are not coplanar, because of the proximity of bulky substituents. A similar phenomenon occurs, for example, with 2,4,6-tri-t-butyltoluene (XII),[56] or 1,2,4,5-tetra-t-butylbenzene (XIII),[57] which have the form of a tub:

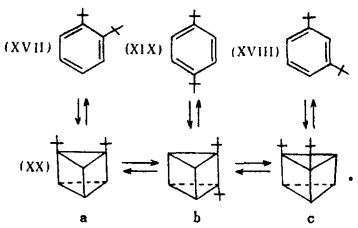


The non-planar structure of the molecule (X) must lower the stability of this hydrocarbon in comparison with other aromatic compounds that do not contain sterically hindered alkyl groups and thereby facilitate its conversion into the strained bicyclic form (XI).[6]

A number of papers deal with the displacement of alkyl groups in benzene homologues under the action of ultraviolet light[58-60]. Using an isotope marker, Kaplan and coworkers[60] established that isomerisation of 1,3,5-trimethylbenzene (XIV) to 1,2,4-trimethylbenzene (XV) (30°, λ = 2537 Å) proceeds not as a result of 1,2-shift of the methyl group, as it might well do, but by a change in the positions of the carbon atoms in the ring — in (XV), as well as in (XIV), the methyl groups are attached to labelled carbon atoms in the ring. This change is said to be effected by the equilibrium compound (XIV) and the three "Dewar isomers" (XVI, a, b, and c) which is rapidly established under ultraviolet irradiation; the "Dewar isomers" are, in turn, in equilibrium with the initial and final compounds.

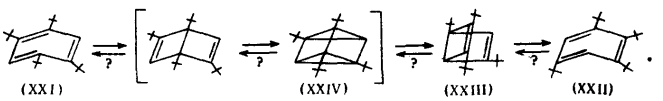


Because of the great strain set up in the molecule by the proximity of the t-butyl radicals, when *o*-di-t-butylbenzene (XVII) is irradiated with ultraviolet light, it is converted into an equilibrium mixture of the *meta*- and *para*-isomers (XVIII) and (XIX) (in the ratio 1 : 4):



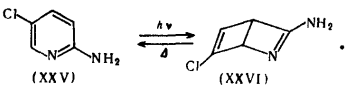
Burgstahler and coworkers[59,61], who described this phenomenon, suggest that the conversion of (XVII) into (XVIII) and (XIX) is accomplished by valence isomerisation of the initial molecule, at first into homologues of "Ladenburg benzene" (XX, a, b, and c) and then into the observed reaction product.

Later, Arnett and Bollinger[62] observed that when 1,2,4,5-tetra-t-butylbenzene (XXI) is irradiated with ultraviolet light, 1,2,3,5-tetra-t-butylbenzene (XXII) is formed, together with the "Dewar isomer" 1,2,3,5-tetra-t-butylbicyclo[2,2,0]hexa-2,5-diene (XXIII).[62] In the opinion of these workers, the fact that irradiation of the highly strained compound (XXI) gives the still more highly strained compound (XXII) excludes any other isomerisation mechanism except intramolecular reorganisation of bonds with the intermediate formation of the homologue of "Ladenburg benzene", "tetra-t-butylprismane" (XXIV) according to the following scheme:

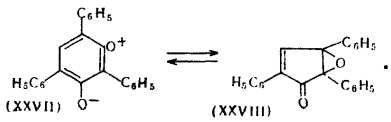


The reversibility of the valence isomerisation (XXI) $\rightleftharpoons$ $\rightleftharpoons$ (XXII) in this example has not yet been demonstrated.

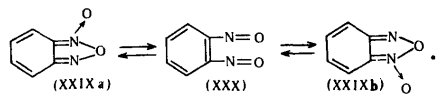
Reversible valence isomerisation similar to the isomerisation of benzene homologues to bicyclohexadiene homologues is observed in a number of heterocyclic compounds. Thus, illumination with sunlight converts 2-amino-5-chloropyridine (XXV) into the bicyclic isomer (XXVI), which was characterised by its ultraviolet and NMR spectra[63,64]. When set aside at room temperature, the isomer (XXVI) is reconverted into the initial compound; this is indicated by the reappearance of the characteristic absorption spectrum of the aminochloropyridine in the ultraviolet region:



Another type of valence isomerisation occurs with triphenylpyrilium oxide (XXVII),[65] which is converted on irradiation with light of wavelength greater than 4500 Å into 1,2,4-triphenylcyclopentadienone oxide (XXVIII) (see also other work[66-68]). On irradiation with light of wavelength 3200–3930 Å, the latter is converted into the starting compound (XXVII).



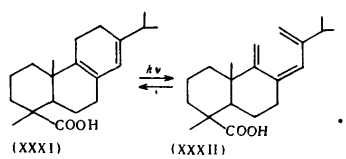
Instances of ring-chain valence tautomerism of heterocycles are known[69-72]. Thus, it was established[70,71] from the temperature dependence of the NMR spectrum of ^{17}O in benzofurazan oxide (XXIX) between -60° and +100° that this compound is in a state of rapid valence-tautomeric conversion, which includes an *o*-dinitrosobenzene (XXX) stage:



(XXIXa) (XXX) (XXIXb)

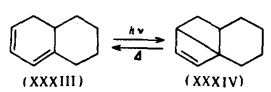
The life period of each tautomer is so short that none of them can be isolated in the pure state.

Under the action of light, compounds that have the 1,3-cyclohexadiene-ring system as a component undergo reversible valence isomerisation, which may proceed in two directions[73]. In the first, the six-membered ring containing two conjugated double bonds opens to form a hexa-1,3,5-triene grouping. In the other, a second smaller ring is formed inside the cyclohexadiene ring. An example of a conversion of the first type is the equilibrium between palustric acid (XXXI) and the triene (XXXII), which is set up by the action of light[74] (see also other work[26,75-81]):



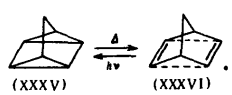
(XXXI) (XXXII)

A conversion of the second kind occurs when 1,2,3,4,9,10-hexahydronaphthalene (XXXIII) is irradiated with ultraviolet light; this compound then isomerises to the tricyclic hydrocarbon (XXXIV). When (XXXIV) is heated to 150°, (XXXIII) is regenerated[77] [see above, conversion (IV) ⇌ (III), also Dauben and Fonken[82], and Prinzbach and coworkers[83]]:



(XXXIII) (XXXIV)

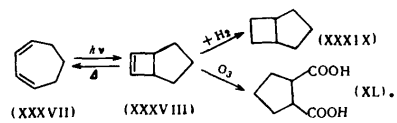
There is great interest[84-87] in the reversible isomerisation of quadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]heptane (XXXV) to norbornadiene (XXXVI):



(XXXV) (XXXVI)

The existence of interaction between the 2 and 6, and between the 3 and 5 carbon atoms of the excited norbornadiene molecule facilitates this reaction[88].

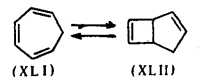
On ultraviolet irradiation, cyclopenta-1,3-diene (XXXVII) is converted into bicyclo[3,2,0]hept-6-ene (XXXVIII), the structure of which has been proved in an exhaustive manner (see scheme). When the photoisomer (XXXVIII) is heated to 400°, the reversible conversion (XXXVIII) → (XXXVII) occurs[89]:



(XXXVII) (XXXVIII) (XXXIX) (XL).

Some derivatives of cycloheptadiene undergo an analogous reversible photoisomerisation[90-93].

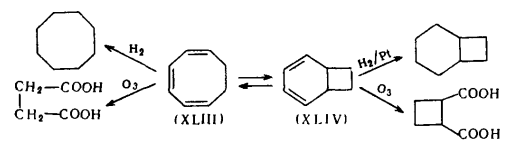
Under the action of light, cycloheptatriene, or tropilidene (XLI), isomerises to bicyclo[3,2,0-[hepta-2,6--diene (XLII);[89] tropilidine derivatives behave in the same way[30,94-96]. At high temperature, the bicyclic isomer (XLII) is converted into tropilidene:



(XLI) (XLII)

A great many cyclic polyenes undergo the so-called intracyclic diene synthesis, in which one double bond plays the part of a dienophile, and the other that of a conjugated diene system[97]. In turn, the bicyclic "adducts" obtained by this reaction can undergo retrodiene decomposition to give the starting compound; it not infrequently happens that both these reactions of cyclic polyenes occur under the same conditions, and as a result two valence-isomeric compounds are found to be in a state of tautomeric equilibrium.

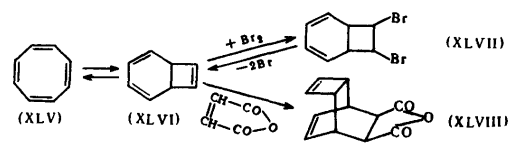
The most striking example of valence tautomerism is intracyclic diene synthesis and decomposition is the equilibrium between bicyclo[4,2,0]octa-2,4-diene (XLIV) and cyclo-octa-1,3,5-triene (XLIII), which is established at 100°.[97-101] The equilibrium position corresponds to a concentration of 15% of the bicyclic and 85% of the monocyclic tautomer. Both tautomers can be obtained in the pure state, and their structures have been proved conclusively (see scheme); when heated to 100° each of the tautomers gives the same mixture, (XLIII) + (XLIV):



(XLIII) (XLIV)

The activation energy for this conversion is 27.1 kcal × × mole^{-1}.[102]

The cyclo-octatetraene (XLV)–bicyclo[4,2,0]octatriene (XLVI) system is an example of widely displaced equilibrium:



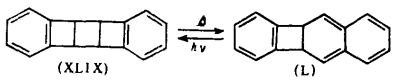
(XLV) (XLVI) (XLVII) (XLVIII).

It has long been known that cyclo-octatetraene reacts in two ways[103-109]. Thus, hydrogenation of (XLV) gives cyclo-octane, but halogenation and diene synthesis give the derivatives (XLVII) and (XLVIII) respectively, the formation of which would be expected on the basis of the tautomeric bicyclo-octatriene (XLVI). However, up to recently no reliable proofs that this tautomer really existed could be adduced. In 1964, the kinetics of the diene synthesis of cyclo-octatetraene with a number of dienophiles of different activity was studied[110]. The results showed that valence tautomerism does in fact exist between cyclo-octatetraene and bicyclo-octatriene, but the concentration of the bicyclic form is only about 0.01%. Nevertheless it is this form that determines the course of the diene-synthesis reaction.

Later, Vogel and coworkers succeeded in obtaining bicyclo-[4,2,0]octatriene (XLVI) in the pure state[111] by elimination of bromine from the dibromide (XLVII) at -78° with the aid

of the disodium derivative of phenanthrene. The structure of the hydrocarbon (XLVI) obtained in this way was confirmed by a number of chemical and spectroscopic data. At room temperature this hydrocarbon spontaneously isomerises to (XLV); the activation energy of the isomerisation is 18.7 kcal mole^{-1}.

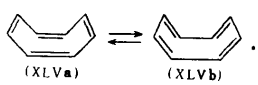
Derivatives of bicyclo[4,2,0]octatriene that are stable at room temperature are known [112,113]. On irradiation, some of them undergo valence isomerisation to the corresponding tricyclo[4,2,0,$0^{2,5}$]octadiene (XLIX) derivatives, for example [103]:



(XLIX) (L)

See also Wittig and Weinlich [112], Criegee and coworkers [113], and Keller and coworkers [114]. When (XLIX) is heated to 200°, (L) is regenerated.

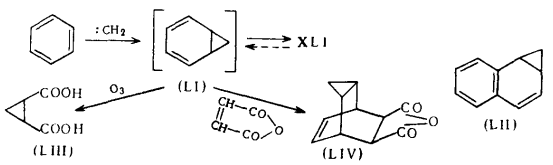
The results of a recent study of the temperature dependence of the NMR spectrum of cyclo-octatetraene led Anet and coworkers to the conclusion that there is a rapid displacement of single and double bonds within the cyclo-octatetraene ring [115]:



(XLVa) (XLVb)

The conversion (XLVa) $\rightleftharpoons$ (XLVb) does not lead to the formation of a new compound; it is an example of what is termed degenerate valence tautomerism. It is doubtful if degenerate valence tautomerism could be recognised by a chemical method, but it nevertheless has a real existence. Other examples of this kind of tautomerism will be given below. The activation energy of the conversion is 12 kcal × × mole^{-1}.

The problem of the existence of valence tautomerism in the tropilidene (XLI)–norcaradiene (LI) system has still not been solved [116,117]. Unsubstituted norcaradiene should be formed by the action of methylene on benzene, in the same way as benzonorcaradiene (LII) is obtained in the analogous reaction with naphthalene [118]:

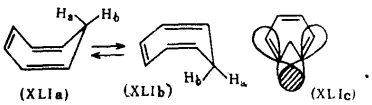


However, when diazomethane was decomposed in benzene, tropilidene was obtained instead of norcaradiene [119]. This may be explained by the isomerisation of norcaradiene to tropilidene immediately it is formed.

It was further noted that tropilidene has some anomalous properties: in oxidations it gives the compound (LIII), and in the diene-synthesis it gives the compound (LIV), both of which contain the three-membered ring [120–123]. Two possible explanations of the results of these reactions have been put forward [120]: either the reagent causes isomerisation of tropilidene to norcaradiene, which then reacts in the normal way, or even in the absence of the reagent the initial tropilidene contains norcaradiene as impurity, with which it is in a state of valence tautomerism. Up to now the presence of norcaradiene has not been detected in the reactions enumerated above, nor could it be shown that it is formed as an intermediate.

Spectroscopic data [123–128] indicate that if the equilibrium of the two forms actually exists, it must be almost wholly displaced in the direction of tropilidene; in any case, the concentration of the bicyclic tautomer does not exceed 0.01%. The preponderance of tropilidene can easily be accounted for: approximate calculations show that this hydrocarbon must be more stable than norcaradiene by 12 kcal mole^{-1}. [129]

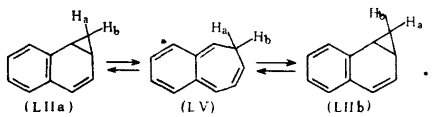
A study of the NMR spectrum of tropilidene at different temperatures [125,126,130], and X-ray studies of (XLI) and some of its crystalline derivatives [131,132] have shown that this hydrocarbon has a non-planar molecule in the form of a tub, with alternate single and double bonds. Even at room temperature tropilidene undergoes ring inversion (XLIa) $\rightleftharpoons$ $\rightleftharpoons$ (XLIb).



(XLIa) (XLIb) (XLIc)

The shape of the ring in this compound is such that the π-electrons of the carbon atoms at positions 1 and 6 partly overlap under the "tub", giving rise to an unusual π-bond (XLIc). [132] The existence of such a bond might explain the dual reactivity of tropilidene (reactions with transfer of reaction centre); however, the existence of valence tautomerism between the quasiaromatic compound (XLI) and norcaradiene is considered to be possible in principle [133]. It is clear that the detection of the bicyclic tautomer when it is present in insignificant concentration is no easy task.

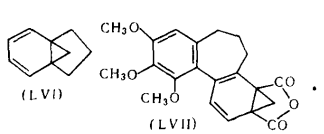
Under ordinary conditions, the benzonorcaradiene (LII) mentioned above is stable. This appears to be due to the high energy content of the valence-isomeric benzocycloheptatriene (LV), resulting from the formation of an *ortho*--quinoid structure [134]:



(LIIa) (LV) (LIIb)

Nevertheless, at temperatures of the order 150–180° a change of position is noted in the signals of the methylene--group protons in the NMR spectrum of benzonorcaradiene. According to Vogel and coworkers [135,136], this indicates that at high temperature a state of equilibrium is set up between the *exo*- and *endo*-forms of benzonorcaradiene, (LIIa) and (LIIb), the compound (LV) being formed as an intermediate [135,136]. The activation energy for the conversion of (LII) into (LV) was calculated from the temperature dependence of the chemical shifts of H_a and H_b; the value found was 19.4 kcal mole^{-1}.

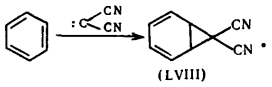
Norcaradiene derivatives fully resistant to isomerisation into the corresponding tropilidene derivatives may be obtained by linking the 1- and 6-carbon atoms of norcaradiene by a three-atom bridge, as in (LVI) [15] or (LVII) [137] (compare Knox and coworkers [138]):



(LVI) (LVII)

Recently it was found that the introduction of two nitrile groups at the seventh carbon atom of norcaradiene also makes

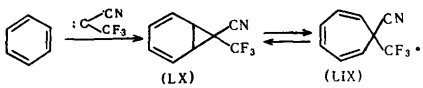
this system stable [139]. The synthesis of 7,7-dicyanonorcaradiene (LVIII) is shown by the following scheme:



(LVIII)

The structure of (LVIII) has been proved by ultraviolet and NMR spectra and by chemical methods.

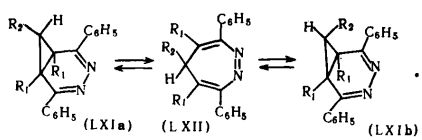
In contrast to (LVIII), 7-cyano-7-trifluoromethylcycloheptatriene (LIX), which is obtained by reaction of the corresponding carbene with benzene, is in equilibrium at room temperature with 7,7-disubstituted norcaradiene (LX): [140]



(LX) (LIX)

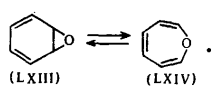
The preparation of stable derivatives of norcaradiene, and the existence of valence tautomerism between (LII) and (LV), and between (LIX) and (LX), definitely confirm the hypothesis of valence tautomerism in the norcaradiene-tropilidene system.

In 1963, Maier prepared nitrogen-containing analogues of norcaradiene (LXI) [141] and was subsequently [142,143] able to show the existence of a tautomeric equilibrium between (LXI) (R_1 = H, R_2 = CH_3) and the monocyclic form (LXII). The concentration of the latter, however, is so low that the compound (LXII) cannot be detected by chemical or by spectroscopic methods. The existence of equilibrium in the system (LXI) $\rightleftharpoons$ (LXII) can only be deduced on the basis of *exo/endo*-transfer of the 7-methyl group in the system (LXIa) $\rightleftharpoons$ (LXIb), which has been demonstrated by means of NMR spectroscopy:



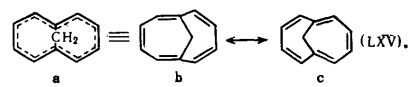
(LXIa) (LXII) (LXIb)

Valence tautomerism, analogous to the conversion (LXI) $\rightleftharpoons$ (LXII) has also been described in a number of three-membered heterocycles [144,145]. The position of the NMR signals and the ultraviolet absorption spectrum of benzene oxide (LXIII) [1a,5a-dihydrobenzoxiran] suggest that this compound is in a state of mobile equilibrium with oxepin (LXIV) (compare Vogel and coworkers [146]):



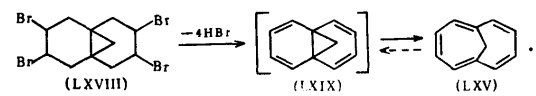
(LXIII) (LXIV)

Vogel and Roth [147] (see also Vogel and coworkers [146]) utilised the ability of norcaradiene to undergo spontaneous valence isomerisation with opening of the three-membered ring in the synthesis of 1,6-methanocyclodecapentaene§ (LXV). This hydrocarbon is of interest because it contains 10 π-electrons and according to Hückel's rule should be aromatic in character¶. In this case its structure would be represented by formula (LXVa) with delocalised double bonds, or, in terms of resonance theory, by the superposition of the two structures (LXVb) and (LXVc):



a b c (LXV).

The synthesis of (LXV) is effected according to the following scheme:



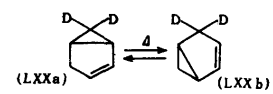
(LXVIII) (LXIX) (LXV)

When alkali acts on the tetrabromo-compound (LXVIII), 9,10-dihydro-9,10-methanonaphthalene (LXIX) should be obtained. However, this hydrocarbon contains the unstable norcaradiene grouping and might be expected to isomerise to (LXV) immediately it is formed. Moreover, the possibility of the formation of an equilibrium mixture of both compounds must be considered.

The ultraviolet and NMR spectra of the reaction product provide evidence against the structure (LXIX). The presence of a ring current in the molecule [147] and the chemical properties of the reaction product, for example, its tendency to undergo substitution reactions [151], are some indications of its aromatic character. However, the possibility of valence tautomerism between (LXIX) and (LXV) cannot be entirely ruled out.

The tendency of norcaradiene and related structures to isomerise to tropilidene and its derivatives is due to strain on the three-membered ring [2,3]: the energy for the breaking of the C–C bond of cyclopropane is less by 19 kcal mole^{-1} than the energy required to break the single bond in ethanol (81 kcal mole^{-1}). A further reduction in the C_1–C_6 bond energy in norcaradiene in comparison with saturated hydrocarbons occurs, because after this bond has been broken, two allyl radicals, capable of conjugation and therefore relatively stable, are formed. This reduces the C_1–C_6 bond energy by a further 2.22 kcal mole^{-1} (where 22 kcal mole^{-1} is the stabilisation energy of one allyl radical). As a result, the activation energy for the isomerisation of norcaradiene to tropilidene is only ~20 kcal mole^{-1}. [3,135]

Because of the favourable occurrence of a three-membered ring in conjunction with a double bond, valence isomerisation of compounds containing the vinylcyclopropane grouping is found to be very common [31,76,83,152–155]. An interesting example of this kind is the conversion of 6,6-dideuterobicyclo[4,1,0]hex-2-ene (LXXa) into 2,2-dideuterobicyclo-[4,1,0]hex-3-ene (LXXb) by heating to 225°. [3] It may be noted that this conversion only occurs because one of the carbon atoms of the initial molecule is labelled with deuterium; the isomerisation is degenerate. The NMR spectrum may be used to distinguish the initial molecule (LXXa) from the mixture of valence isomers (LXXa) and (LXXb) obtained after heating:

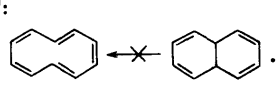


(LXXa) (LXXb)

Compounds containing two double bonds and a three-membered ring undergo valence isomerisation still more easily [118,156–165], as shown, for example, by the isomerisation of 1,2-divinylcyclopropane (LXXI) to cyclohepta-1,4-diene (LXXII); [3,33] the *cis*-isomer of this hydrocarbon is

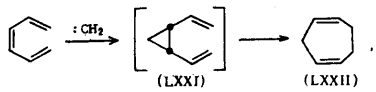
§ Bicyclo[4,4,1]undeca-1,3,5,7,9-pentene (Ed. of Translation).

¶ Attempts to prepare unsubstituted cyclodecapentaene (LXVI) by valence isomerisation of 9,10-dehydronaphthalene (LXVII) were not successful [148–150]:



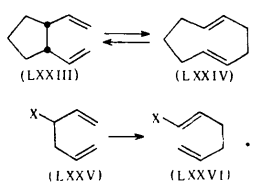
(LXVI) (LXVII)

converted into (LXXII) immediately it is formed from hexatriene and methylene at -40°:



In most instances the conversion turns out to be irreversible, because of the great difference in free energy between the initial and final compounds. This difference is less for divinylcyclobutane than for divinylcyclopropane [33], but the free energy of divinylcyclopentane (LXXIII) is found to be even somewhat less than that of the valence-isomeric cyclononadiene (LXXIV). Vogel and coworkers found that at 200° (LXXIII) and (LXXIV) are in a state of dynamic equilibrium [191]. The equilibrium position corresponds to a concentration of 95% of divinylcyclopentadiene and 5% of cyclononadiene.

The valence isomerisation of divinylcycloalkanes is a special case of the well-studied thermal isomerisation of 1,5-dienes called the Cope rearrangement [166,167] (LXXV)–(LXXVI):

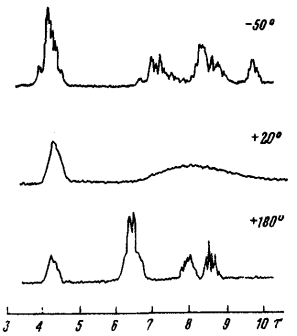


It is known that neither ionic nor radical intermediates are formed in the course of this reaction [2,3]: the reaction is effected via a cyclic transition state in which old bonds are broken and new bonds are simultaneously formed. Atoms or atomic groups do not migrate during the reaction; the Cope rearrangement is a typical example of valence conversion. However, in accordance with the definitions of rearrangement and isomerisation (see p. 560), these reactions should not be called rearrangements but isomerisations. The Cope isomerisation has been the subject of several reviews [2-4,33,168]; for this reason, we shall confine ourselves to a reference to some new examples of valence conversions of this type [52,53,169-179].

The valence tautomerism of homotropilidene, or bicyclo[5,1,0]octa-2,5-diene (LXXVII), and of other compounds containing the homotropilidene grouping occupies a special position among valence isomerisations. A special feature of these conversions is that they are degenerate (the initial and final stages of the conversion are indistinguishable) and that they occur very rapidly. It is concluded that tautomerism actually occurs, because the NMR spectra of homotropilidene and its derivatives undergo reversible changes with change of temperature, while the infrared spectra remain unchanged.

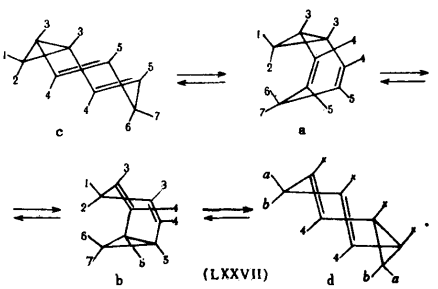
At -50° the NMR spectrum of homotropilidene [3,168,180] shows signals corresponding in position and intensity to the seven types of protons in homotropilidene (see Figure); at this temperature the rate of valence tautomerism of homotropilidene is relatively low.

When the temperature is increased, the conversion (LXXVIIa) ⇌ (LXXVIIb) is accelerated. Tautomerism leads to an exchange of the positions of protons, H_1 with H_7, H_2 with H_6, and H_3 with H_5. With very rapid mutual transfers (+180°), the half-life of each tautomer does not exceed 0.004 s; the H_1 and H_7 protons become indistinguishable in the NMR spectrum and give only one signal of type $2H_a$. Similarly,



NMR spectrum of homotropilidene.

H_2 and H_6 form one signal $2H_b$. Rapid mutual conversions of $2H_3$ and $2H_5$ lead to one new $4H_x$ signal. Only the $2H_4$ signal retains its position corresponding to two vinyl protons. Thus, from the point of view of NMR spectroscopy, the fairly rapid valence tautomerism of homotropilidene leads from a compound with seven types of protons to a compound with four types.



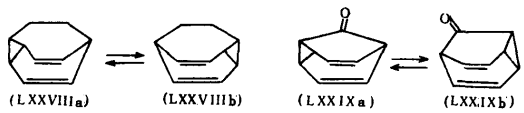
Because of the existence of rapid degenerate valence tautomerism, a single formula does not represent the structure of homotropilidene over a long time interval. Homotropilidene belongs to a group of compounds with what is termed a fluctuating structure [180].

Quite a number of compounds with fluctuating structures are now known; these include: tricyclo[3,3,2,$0^{4,6}$]deca-2,7-diene (LXXVIII), [181] tricyclo[3,3,1,$0^{2,8}$]nona-3,6-dien-9-one or barbaralone (LXXIX), [182] tricyclo[3,3,2,$0^{1,8}$]deca-2,5,9-triene or bullvalene (LXXX), [181,183-185] and also some derivatives of these [186-191].

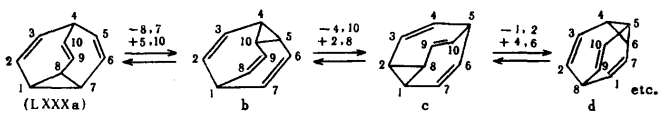
Homotropilidene exists in two forms, the cisoid (LXXXVIIa) and the transoid (LXXVIIc), and only the cisoid form undergoes isomerisation [180], but with barbaralone and bullvalene the unsuitable transoid conformation of the molecule is excluded, and valence isomerisation may be expected to occur still more readily. The question than arises whether a limit has been reached at which two separate classical structural formulae cease to correspond to two separate potential energy minima (each with its own set of vibrational levels) and are converted into two limiting structures representing the same compound. Here the concept of tautomerism would have to be equated with the concept of mesomerism.

A study of the NMR spectrum of barbaralone has shown that at -60° this ketone exists in the form of two tautomers. At higher temperatures, the spectrum shows some intermediate proton positions, which are occupied during the

rapid transformation from one tautomer to the other. The activation energy of the valence-tautomeric conversion of barbaralone is only 8.1 kcal mole^{-1}.



As would be expected, bullvalene (LXXX), which was predicted in 1962 by Doering [168] and synthesised in 1963 by Schröder [183,184], has only one signal in its NMR spectrum at 100°. This means that, at this temperature, because of very rapid valence-tautomeric conversions, all the protons, and therefore all the carbon atoms, of the molecule become, as it were, equivalent. It can be shown by means of successive Cope isomerisations, associated with the rupture of any of the three C–C bonds of the three-membered ring (the molecule has a threefold axis of symmetry), that each carbon atom can occupy the position of any other atom, for example:



It has been calculated that there are more than a million different mutual arrangements of the carbon atoms in bullvalene, and all these combinations (permutations [186]) occur in the molecule over a short time interval, comparable with the relaxation period of the nuclear spins of the protons linked with these carbon atoms. Thus, the carbon atoms of bullvalene are not in "fixed" positions but move at relatively high speed over the "surface" of the molecule [168]. These displacements of atoms do not, however, lead to a change in the structure of the compound.

It should be noted that the high rate of bullvalene valence--tautomeric conversions must, however, not be regarded as evidence that all the 1 209 600 tautomers that undergo mutual conversion can be obtained one from the other at the same rate, since the conversion of one into another occurs in many stages – for example, (LXXXa) into (LXXXd). [186]

The question whether bullvalene is an equilibrium mixture of a tremendous number of valence isomers undergoing rapid conversion or an individual compound which is a resonance hybrid of a number of electronic structures has been decided with the aid of the theory of groups: ten points cannot be arranged on the surface of a sphere in such a way that a geometrical figure completely symmetrical in three dimensions is obtained. It is quite clear that only with such a construction would bullvalene have ten really equivalent carbon atoms. Since this construction is impossible, it follows that even at high temperature bullvalene is a mixture of 1.2 million irregular polyhedra, rapidly being converted into one another. The minimum energy of this system is represented not by one average state but by 1.2 million states identical in energy (degenerate), but separated from one another by an energy barrier (11.8 kcal mole^{-1} [185]). In other words, in bullvalene we also have an instance of valence tautomerism, and not of mesomerism.

The number of examples of reversible valence isomerism has increased to such an extent in recent years that it would be difficult to give all the examples in a single review. However, even the foregoing presentation will be quite sufficient to attract the attention of chemists to this new interesting type of isomerisation†.

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THE CHEMISTRY OF THE B_3–B_9 BORON HYDRIDES

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I. INTRODUCTION

The boron hydrides occupy a special place among the various classes of boron compounds, being typical representatives of electron deficient compounds. The study of their structure and reactivity has been the largest contribution to the theory of the chemical bond. The boron hydrides also find practical application as fuel additives, lubricants, neutron absorbers, intermediates in the production of polymers with special properties, selective reductants, etc. The first series of boron hydrides were obtained by Stock at the beginning of the XXth century after his development of special apparatus suitable for work with thermally unstable compounds sensitive to moisture and air. The chemistry of the boron hydrides has begun to develop extremely rapidly in the last decade, and now about 50 years after their discovery, the structure and chemical properties of a series of stable and unstable boron hydrides and their derivatives have been rather well studied.

The present article is a brief review of most of the investigations on the structure and chemical reactions of the boron hydrides containing from three to nine boron atoms in the molecule, the main attention being directed to the chemical properties of these compounds. The literature cited is mainly up to 1st July 1964. The problem of the structure of the boron hydrides received detailed discussion in Lipscomb's book [1], in which the chemical reactions of individual boron hydrides received comparatively little attention. The structure and chemical properties of diborane were reviewed by Mikhailov [2] and the chemistry of decaborane by Stanko and coworkers [3]. Some problems of boron hydride chemistry have been briefly discussed in the book by Samsonov and coworkers [4].

II. GENERAL CONSIDERATIONS ABOUT THE NATURE OF THE BONDS IN BORON HYDRIDES

Lipscomb proposed and developed the modern theory of the structure of boron hydrides, explaining their special properties on the basis of the concept of three-centre bonds. As is well known, with the usual covalent (two-centre) bond the two atoms have two orbitals (one bonding and one antibonding) in common and one electron from each atom; the pair of electrons fill the bonding orbital and form a two-centre bond. In the formation of a three-centre bond three atoms

have three orbitals in common use, in the interaction of which one bonding and two antibonding orbitals are formed. A pair of electrons fills only the bonding orbital. These types of bond are instances of the general type of multi-centre bonds. In considering the structure of the boron hydrides studied by him and other investigators, Lipscomb arrives at the following fundamental conclusions.

1. The hybrid orbitals of the boron atoms belong to the usual types of hybridisation: tetrahedral sp^3 or trigonal planar sp^2. The nature of the hybridisation is determined by energetic factors favourable to the formation of the most stable bonds. The hydrogen atoms use only the 1s-orbitals.

2. Each terminal B–H bond is a "normal" two-centre bond; on account of the very small difference in electronegativity of the boron and hydrogen atoms these bonds are considered non-polar. Each boron atom has not more than two terminal B–H bonds.

3. For the formation of the skeleton of the boron hydride molecule, bonds of four types are used in addition to the terminal B–H bonds; (a) B–H–B bridging three-centre bonds of "open" type; the electron density in this type of bond is concentrated along the lines joining the atoms; (b) two-centre covalent B–B bonds; (c) "open" three-centre B⟨B⟩B bonds, in which the π-orbital of the central boron atom and two σ-orbitals of the outer boron atoms are used; (d) the "central" three-centre bond B⟨B⟩B, using the σ-orbitals of all three boron atoms; the electron density is concentrated near the centre of the triangle connecting the boron atoms.

4. The orbitals and electrons of the boron atoms are so distributed as to first satisfy the requirements of the terminal B–H bonds and bridging B–H–B bonds. The remaining orbitals and electrons are used for bonds with the other boron atoms, which form the molecular skeleton. The molecules of the boron hydrides are constructed from a few "structural units" and for a given empirical formula the number of possible structural units and bonds is strictly limited and can be determined by use of the topological theory developed by Lipscomb.

5. The following are the most apparent principles in the geometry of most boron hydride molecules: the arrangement of the boron atoms as fragments of octahedra or icosahedra; the presence of hydrogen bridge atoms in the open parts of the molecule; coordination numbers of 5 or 6 for the boron atoms; and a marked tendency to the formation of triangles of boron atoms. Triangles formed by a bridge hydrogen and the two boron atoms adjacent to it, and triangles of boron atoms, can replace one another on going from one member of the series to another.

III. TRIBORANE

1. Structure

Triborane itself, B_3H_9, has not been obtained, owing to its instability. In several studies [5-8] the formation of B_3H_9 or B_3H_7 as intermediates in the conversion of diborane into higher boron hydrides is assumed, and also in the action of HCl on NaB_3H_8. [9] The B_3H_9 molecule contains 18 electrons and 21 orbitals. Lipscomb [10,11] has proposed the most satisfactory structure for B_3H_9, in which each boron atom forms two terminal B–H bonds; three BH_2 groups are connected by bridging hydrogen atoms, forming a ring, similar to cyclopropane (Fig. 1; one of the terminal hydrogen atoms of the BH_2 groups is not shown).

Triborane derivatives in the form of complexes of neutral, $B_3H_7.L$ (where L is a Lewis base), or ionic, $X^+B_3H_8^-$, type have been isolated and studied in detail. Their structure was established by X-ray diffraction and by NMR spectra.

Nordman and Reimann [12,13] showed that the complex $NH_3.B_3H_7$ has two crystalline modifications: low-temperature (monoclinic crystals with group symmetry $P2_{1/n}$, unit-cell parameters a = 10.40, b = 4.824, c = 9.997 Å, β = 115.2°), which is converted at 297.0°K into the high-temperature form with partly disordered crystals (tetragonal with unit-cell parameters a = 6.11, c = 6.57 Å). The low-temperature modification of $NH_3.B_3H_7$ has been studied in sufficient detail and the positions of the B, N, and H (bound to B) atoms have been accurately determined; those of the H atoms bound to N have not, probably because of their rapid random motion in relation to the B–N bond. These authors, and also Kodama and Parry [14], ascribed to the complex $NH_3.B_3H_7$ the structure shown in Fig. 2.

The following interatomic distances have been determined (in Å): $B_{(1)}-B_{(2)}$ = 1.744 ± 0.005, $B_{(1)}-B_{(3)}$ = 1.820 ± ± 0.006, $B_{(2)}-B_{(3)}$ = 1.803 ± 0.006, $N-B_{(3)}$ = 1.581 ± 0.003, $B-H_{terminal}$ = 1.13 ± 0.07, $B_{(1)}-H_{(3)}$ = 1.23 ± 0.03, $B_{(2)}-H_{(3)}$ = = 1.39 ± 0.05, $B_{(3)}-H_{(6)}$ = 1.12 ± 0.03, $B_{(2)}-H_{(6)}$ = 1.75 ± 0.03; the angles between bonds are: $\angle NB_{(3)}B_{(1)}$ = 111.0° ± 0.5°, $\angle NB_{(3)}B_{(2)}$ = 115.3° ± 0.5°, $\angle NB_{(3)}B_{plane}$ = 117.2° ± 0.5°.

The B_3H_7 group is considered to be a fragment of a tetraborane molecule, formed from it in the symmetrical splitting of a bridge bond. A triangle of boron atoms forms two bridge bonds $B_{(1)}H_{(3)}B_{(2)}$ and $B_{(2)}H_{(6)}B_{(3)}$ and one covalent bond $B_{(1)}B_{(3)}$, and the NH_3 group is connected with the $B_{(3)}$ atom and located at an angle of 65° to the plane formed by the boron atoms.

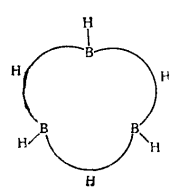


Fig. 1.

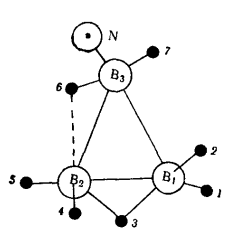


Fig. 2.

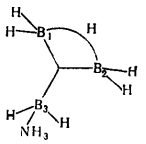


Fig. 3.

Muetterties and coworkers [15], on the basis of the ^{11}B-NMR spectrum of $B_3H_7.O(C_2H_5)_2$ and NaB_3H_8, which showed the identity of all three boron atoms, ascribed to $B_3H_8^-$ and B_3H_7 another type of structure, in which three identical boron atoms are connected by six bridging hydrogen atoms. Furthermore, the molecule contains two hydrogen atoms of another type, each of which is joined to all three boron atoms. Such a structure does not agree with the results of the X-ray analysis of $NH_3.B_3H_7$ [12] and $N(CH_3)_3.B_3H_7$, [10] which show that these molecules do not possess a third-order axis of symmetry. The results on the geometry of $NH_3.B_3H_7$ also agree rather well with the structure shown in Fig. 3. Here the $B_{(3)}-H_{(6)}$ bond is a terminal B–H bond and the $B_{(2)}$ atom is not connected to the $H_{(6)}$ atom. All three boron atoms are connected to one another by a central three-centre bond and each boron atom has two terminal hydrogen atoms. The atoms $B_{(1)}$ and $B_{(2)}$ are linked by hydrogen bridge bonds and a vacant orbital of the atom $B_{(3)}$ is used for a coordinate bond with the nitrogen atom. This structure is supported by the following facts: (1) the length of the $B_{(1)}-B_{(3)}$ bond is appreciably greater than the length of the B–B covalent bond in B_4H_{10} (1.712 Å); (2) the distance between the atoms $B_{(1)}$ and $B_{(2)}$ (1.744 Å) is less than that between the boron atoms joined by hydrogen bridging atoms (1.84 Å); (3) the B_3H_6 distance equals the mean of the terminal B–H bonds whereas B_2H_6 is 0.4 Å greater than the length of the usual bridging bond.

The structure of the ion $B_3H_8^-$ was found by X-ray diffraction and NMR spectra. The X-ray structural analysis [16] of the "diammoniate of tetraborane" $[(NH_3)_2BH_2]^+.[B_3H_8]^-$ at 25° and -100°C shows that the boron atoms in the anion form a triangle of icosahedra with a base of 1.80 Å and sides of 1.77 Å. On the basis of these results the structure shown in Fig. 4 is proposed. $B_{(1)}-B_{(3)} = 1.80$ Å, $B_{(1)}-B_{(2)} = B_{(2)}-B_{(3)} = 1.77$ Å, $B-H_{terminal} = 1.05-1.20$ Å, $B_{(2)}-H_{bridge} = 1.5$ Å, $B_{(1)}-H_{bridge} = B_{(3)}-H_{bridge} = 1.2$ Å.

In the ion $B_3H_8^-$ there is a tautomerism of the hydrogen atoms [10,17] which is facilitated by the increase in the interatomic distances and the presence of a negative charge. This exchange explains the ^{11}B- and ^1H-NMR spectra of NaB_3H_8 [15] and $(CH_3)_4NB_3H_8$ [18] leading to the conclusion that all the boron atoms are equivalent and connected to the same hydrogen atoms, as in $Al(BH_4)_3$, where all the hydrogen atoms are identical.

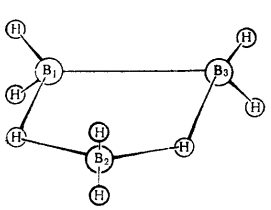


Fig. 4.

2. The Compounds $B_3H_7.L$

The triborane derivative which has been studied in most detail is triborane ammine, $NH_3.B_3H_7$, first obtained by Kodama and coworkers [14] by the action of NH_4Cl on an ethereal solution of NaB_3H_8: [19]

$$NaB_3H_8 + NH_4Cl \xrightarrow[25°]{(C_2H_5)_2O} NH_3.B_3H_7 + H_2 + NaCl\downarrow.$$

However, the compound is obtained in small yield (20–30%) and insufficiently pure; therefore Kodama and coworkers [14,20] also developed a method by which $NH_3.B_3H_7$ is obtained from B_4H_{10} by a series of reactions analogous to those for preparing $NH_3.BH_3$ from B_2H_6. In the action of NH_3 on an ethereal solution of B_4H_{10} at -78°C, the tetraborane undergoes unsymmetrical splitting with the formation of tetraborane diammine, $[(NH_3)_2BH_2]^+[B_3H_8]^-$. On treating this compound with dry HCl in an ethereal solution at low temperature, the reaction:

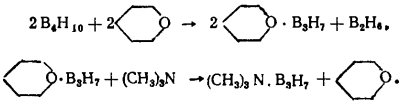
$$[(NH_3)_2BH_2]^+[B_3H_8]^- + HCl + (C_2H_5)_2O \xrightarrow[-78°]{} [(NH_3)_2BH_2]^+Cl^-\downarrow + B_3H_7\cdot(C_2H_5)_2O + H_2,$$

occurs. When the triborane–ether product is treated with ammonia $NH_3.B_3H_7$ is obtained:

$$NH_3 + B_3H_7\cdot(C_2H_5)_2O \xrightarrow[-78°]{(C_2H_5)_2O} NH_3.B_3H_7 + (C_2H_5)_2O.$$

When tetrahydropyran is used instead of ether, pure $NH_3.B_3H_7$ is obtained in 70–94% yield [14]. Triborane–ammonia is a white, crystalline substance, which melts at 73–75°C with weak liberation of hydrogen, and sublimes slowly in a high vacuum. It does not decompose in air and is stable to hydrolysis: the substance is completely hydrolysed only after heating with 6 *N* HCl for several days; the compound dissolves readily in ether, liquid ammonia (at -75°C), and benzene, and is also soluble in acetone and alcohol. The vapour pressure–temperature relation [21], heat capacity, and other thermodynamic constants [22] of $NH_3.B_3H_7$ have been measured, and some of its chemical properties have been studied [14]. It has been found that it does not react with trimethylamine at -78°C, but at 25°C they form $N(CH_3)_3.BH_3$ and an unidentified solid substance, which probably has the composition $HB[N(CH_3)_3]$. [23] NH_3 could not be replaced by $(CH_3)_3N$. When sodium in liquid ammonia acts on $NH_3.B_3H_7$, the B_3H_7 is again destroyed, an equimolecular quantity of hydrogen being released and $NaBH_4$ formed.

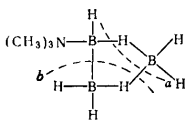
Trimethylamine–triborane $(CH_3)_3N.B_3H_7$ was obtained [24] by a method analogous to that for $NH_3.B_3H_7$:



The yield of $(CH_3)_3N.B_3H_7$ was 65–70%. The compound resembles $NH_3.B_3H_7$ in its properties: when pure it is stable to hydrolysis (for complete hydrolysis heating with 10% HCl for 100 h at 150°C is necessary), it does not decompose on heating to 300°C, does not dissolve in water, is sparingly soluble in ether, and can be recrystallised from alcohol and toluene without decomposition. Crystals of $(CH_3)_3N.B_3H_7$ have two modifications with a transformation point at 209.6°K. The thermodynamic functions of this compound have been determined [24].

Some chemical properties of $(CH_3)_3N.B_3H_7$ have been studied and the instability of the B_3H_7 fragment has been demonstrated. An excess of $(CH_3)_3N$ leads to the splitting of the compound with the formation of $(CH_3)_3N.BH_3$ and $H[B(CH_3)_3]_x$. [25]

A mechanism has been proposed for this reaction[23,26], according to which in the presence of an excess of $(CH_3)_3N$ there is "symmetrical" splitting of the B_3H_7 skeleton, during which the B–H–B bridge bond is broken first (a) with liberation of a BH_3 group and then splitting of the B–B bond occurs with the formation of another BH_3 group (b):



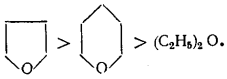
$$\xrightarrow{(CH_3)_3N} 2(CH_3)_3N\cdot BH_3 + HB[N(CH_3)_2]_x.$$

$(CH_3)_3N.B_3H_7$ is also split by triphenylphosphine[27], but there is then incomplete splitting of the triborane skeleton:

$$3(C_6H_5)_3P + (CH_3)_3N.B_3H_7 \xrightarrow[80°]{C_6H_6} [(C_6H_5)_3PBH_2]_2 + (C_6H_5)_3P\cdot BH_3 + N(CH_3)_3.$$

The triborane addition compounds with phosphine Lewis bases were made by a method developed for making $NH_3.B_3H_7$. When $(C_6H_5)_3P$ acts on the addition compound of B_3H_7 with tetrahydrofuran (THF), the THF is displaced and the complex $(C_6H_5)_3P.B_3H_7$ is formed in 54% yield[27]; when $(C_6H_5)_3P$ reacts with $(CH_3)_2S.B_3H_7$ a little $(C_6H_5)_3P.B_3H_7$ is formed and much more $(C_6H_5)_3P.BH_3$. It has been shown that the direction of the reaction depends on the strength of the bond between the ligand and the boron atom in the original complex $B_3H_7.L$: the stronger this bond the greater the destruction of triborane and the quantity of $(C_6H_5)_3P.BH_3$ formed – the strength diminishes in the sequence $(CH_3)_3N > (CH_3)_2S > C_4H_8O$. The displacement of the comparatively weak base tetrahydropyran (THP) from the complex $B_3H_7.THP$ also takes place under the action of a bicyclic phosphite – 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane, $CH_3C(CH_2O)_3P$, in which the complex $CH_3C(CH_2O)_3P.B_3H_7$ is formed with almost quantitative yield[28].

The strength of the B–P dative bond in the coordination compounds of B_3H_7 is less than that of the B–N bond in $(CH_3)_3N.B_3H_7$. Study of the B_3H_7 complexes with various Lewis bases (ethers, NH_3, amines, substituted phosphines, sulphides, etc.) showed that the stability of the $B_3H_7.L$ complexes depends on the coordination capacity of the base. The weaker Lewis bases, such as $(C_2H_5)_2O$, $(CH_3)_2S$, and thiophen, form unstable complexes with B_3H_7, stable only at low temperatures. Strong Lewis bases – pyridine, $(CH_3)_3N$, $(n\text{-}C_3H_7)_3N$ – form stable complexes, but an excess of the amine destroys them, with the formation of BH_3 and polymeric compounds[26]. It has been shown[14] that the stability of the $R_2O.B_3H_7$ complexes decreases in the order:



$$> (C_2H_5)_2O.$$

B_3H_7 is a stronger Lewis acid than BH_3 [26] and displaces the latter from its complexes; therefore under the action of tetraborane the BH_3.amine complexes are converted into B_3H_7.amine complexes with subsequent slow decomposition of the latter into B_2H_6, B_5H_9, and H_2.

3. Properties of Compounds of the Type $X^+.B_3H_8^-$

Triborane compounds with an ionic structure which have been obtained are NaB_3H_8, $(CH_3)_4NB_3H_8$, and $[BH_2(NH_3)_2]^+[B_3H_8]^-$.

Sodium octahydrotriborate(-1) NaB_3H_8 was first obtained by Hough and coworkers[19,29] in yields up to 80% by reaction of sodium amalgam with diborane(6) in ether at room temperature:

$$2Na + 2B_2H_6 \rightarrow NaBH_4 + NaB_3H_8.$$

NaB_3H_8 was the first representative of triborane(9) derivatives of ionic type. It is thermally stable up to a temperature as high as 200°C, readily soluble in ether, methanol, water, and liquid ammonia; it is more stable to hydrolysis than $NaBH_4$; it is solvated in ether, poly- and mono-ether addition compounds having been identified. Dissolution in water and aqueous HCl is accompanied by partial hydrolysis, but complete hydrolysis requires heating with water at 100°C for some days.

NaB_3H_8 is readily formed also by the action of sodium on a solution of "diammoniate of tetraborane" in liquid ammonia[20]:

$$[H_2B(NH_3)_2]^+[B_3H_8]^- + Na \xrightarrow[-78°]{NH_3} NaB_3H_8 + H_2BNH_2 + NH_3 + {}^1/_2H_2.$$

The yield reaches 60–70%. This reaction is analogous to the reaction for producing $NaBH_4$ from "diborane diammine". NaB_3H_8 is obtained in yields of up to 90% by the reaction of $NaBH_4$ with diborane in dimethoxyethane[30].

A neutral triborane complex, $B_3H_7.NH_3$, is formed by the action of ammonium chloride in ether on NaB_3H_8 at 25°C.[14] The behaviour of NaB_3H_8 in this reaction is also analogous to $NaBH_4$, from which $NH_3.BH_3$ is formed under the same conditions.

Gaines and coworkers[31] proposed a rapid and convenient method for preparing $X^+.B_3H_8^-$ compounds by the hydroboration with diborane of the products of the addition of alkali metals to triphenylboron or naphthalene, or by the reaction of metal hydroborates with B_2H_6 in ethereal solution at 100°C. The salt $(CH_3)_4NB_3H_8$ was obtained in high yield. The mechanism of the reaction is unexplained. An interesting path for the preparation of compounds with the $B_3H_8^-$ anion has been proposed, consisting in the stepwise decomposition of decaborane by methanol under strictly controlled conditions[18]:

$$B_{10}H_{14} + 2(C_2H_5)_2S \xrightarrow[80°]{C_6H_6} B_{10}H_{12}\cdot[(C_2H_5)_2S]_2 + H_2; \quad (1)$$

$$B_{10}H_{12}\cdot[(C_2H_5)_2S]_2 + 3CH_3OH \xrightarrow{65°} B_9H_{13}\cdot(C_2H_5)_2S + H_2 + (C_2H_5)_2S + B(OCH_3)_3; \quad (2)$$

$$B_9H_{13}\cdot(C_2H_5)_2S + (CH_3)_4NOH \xrightarrow{C_2H_5OH} B_9H_{12}\cdot(CH_3)_4N + (C_2H_5)_2S + H_2O; \quad (3)$$

$$B_9H_{12}\cdot(CH_3)_4N + 18CH_3OH \xrightarrow{25°} [B_3H_8]^-[(CH_3)_4N]^+ + 6B(OCH_3)_3 + 11H_2. \quad (4)$$

The reaction takes place readily and this method of making $(CH_3)_4N.B_3H_8^-$ (35% yield) is convenient preparatively. $[(CH_3)_4N]^+[B_3H_8]^-$ is a stable, white, crystalline substance, which does not melt below 275°C and is insoluble in cold methanol. It reacts with $(CH_3)_3N.HCl$ in tetrahydrofuran at its boiling point, and forms $(CH_3)_3N.B_3H_7$ in good yield[18]:

$$[(CH_3)_4N]^+[B_3H_8]^- + (CH_3)_3N\cdot HCl \rightarrow (CH_3)_3N\cdot B_3H_7 + H_2 + (CH_3)_4NCl.$$

Hence here, as for NaB_3H_8, the anion $B_3H_8^-$ is converted into the neutral fragment of triborane B_3H_7.

IV. TETRABORANE(10) B_4H_{10}

1. Structure of Tetraborane

Tetraborane was the first of the boron hydrides to be definitely characterised as a chemical compound by Stock and Massenez[32] in 1912. The position of the boron and

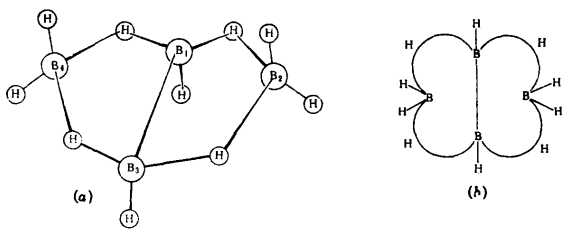


Fig. 5.

hydrogen atoms in B_4H_{10} was unequivocally established by X-ray diffraction [33-35] and electron diffraction [36], also with the aid of ^1H- and ^{11}B-NMR spectra [37]. On the basis of these results for tetraborane the structure shown in Fig. 5 was proposed [10,11]. A quantum-chemical calculation for the molecule was made [38].

The interatomic distances for B_4H_{10} determined by the electron and X-ray diffraction methods differ somewhat from one another. Lipscomb quotes [10] the X-ray results as the more accurate for the distances between the boron atoms and the molecular angles, and the electron diffraction results for the B–H distances. The main data about the geometry of the B_4H_{10} molecule are (in Å): $B_{(1)}-B_{(2)}$ = = 1.842, $B_{(1)}-B_{(3)}$ = 1.712, $B_{(2)}-B_{(4)}$ = 2.800, $B-H_{terminal}$ = = 1.19, $B_{(1)}-H_{bridge}$ = 1.16, $B_{(2)}-H_{bridge}$ = 1.37; the angles (in degrees) are: $\angle B_{(1)}-B_{(2)}-B_{(3)}$ = 56.6, $\angle B_{(1)}-B_{(3)}-B_{(2)}$ = = 61.7, $\angle B_{(2)}-B_{(1)}-B_{(4)}$ = 98, $\angle B_{(1)}-B_{(3)}-H_{(1)}$ = 118; angle between the $B_{(1)}-B_{(3)}-B_{(2)}$ and $B_{(1)}-B_{(3)}-B_{(4)}$ planes = 118.1.

The B_4H_{10} molecule contains two types of boron atom. Each atom of type I forms one two-centre B–H bond and two bridging three-centre B–H–B bonds; furthermore, these two boron atoms are connected to one another by a covalent bond making use of the remaining orbitals and electrons of each atom. The atoms of type II form two two-centre B–H bonds and two three-centre B–H–B bridge bonds, these using all four sp^3-orbitals and all three electrons of the boron atom. The planes of the two triangles formed by the boron atoms are disposed at an angle of 118.1°. The framework formed by the boron atoms of B_4H_{10} can be considered as a fragment of an octahedron or icosahedron as the $B_{(2)}-B_{(1)}-B_{(4)}$ valence angle (98°) is the mean between the angles for an octahedron (90°) and an icosahedron (108°).

Williams and coworkers [37] made a detailed study of and interpreted the ^1H- and ^{11}B-NMR spectra of B_4H_{10}, which confirmed the structure of the molecule shown in Fig. 5. The ^{11}B-NMR spectrum contains a triplet in the weak field region corresponding to the BH_2 groups, and a doublet in the strong field region, corresponding to BH groups; the interpretation of such a doublet structure as a consequence of the $^{10}B-^{11}B$ interaction [37] seemed incorrect, as such interaction is not observed in ^{11}B-NMR spectra of deuterated tetraborane [39]. The ^1H-NMR spectrum of tetraborane shows the presence in it of two types of terminal hydrogen atoms and bridging hydrogens.

The determination of the dipole moment of B_4H_{10}, [38,40] 0.56 ± 0.1 D (in benzene) shows that all the boron atoms are electrically neutral; the slight polarisation of the molecule is due to second-order effects.

2. Preparation of Tetraborane

Tetraborane(10) was first obtained by the action of HCl on magnesium boride [32]:

$$Mg_3B_2 + HCl \rightarrow B_4H_{10} + MgCl_2.$$

This method gives a negligible yield (~ 1%) of a contaminated product. Subsequently several other methods for preparing it were developed. Stock and his coworkers studied the decomposition of several metal borides with various mineral acids [41] and found [42] that the yield is somewhat better in the decomposition of beryllium boride by hydrochloric acid (~ 1.5–2%) and pure B_4H_{10} is obtained (it does not contain silicon hydrides as impurity). Wiberg and Schuster [43] found that when magnesium boride (or a mixture of magnesium and boron trioxide) is decomposed by 8 N H_3PO_4 tetraborane is obtained in ~ 11% yield:

$$B_2O_3 + Mg \rightarrow Mg_3B_2;\ Mg_3B_2 + H_3PO_4 \rightarrow B_4H_{10} + Mg_3(PO_4)_2.$$

In later work [44] it was shown that in this way B_4H_{10} can be obtained in yields of up to 14.5%. Tetraborane was prepared [45] from B_2H_5I and sodium amalgam in 30% yield:

$$2\,B_2H_5I + 2\,Na \xrightarrow[-35°]{} B_4H_{10} + 2\,NaI.$$

However, the method is not very suitable for obtaining comparatively large amounts of tetraborane on account of the instability of B_2H_5I.

After the development of a method of making diborane from boron halides and hydrogen in an electric discharge [46], tetraborane began to be made by the pyrolysis of B_2H_6, initially through the intermediate stage of converting it into B_5H_{11} (100°C, 10 min) and the pyrolysis of the latter [47], and later by direct pyrolysis of B_2H_6 at 180°C and reduced pressure (450 mmHg). [48] Pyrolysis of diborane at elevated pressure (50 atm, 50–75°C) leads to the production of B_4H_{10} in yields of 20–35%. [49] All these methods had various drawbacks. In 1958 a convenient laboratory method for obtaining B_4H_{10} or B_5H_{11} (depending on the reaction conditions) by the pyrolysis of B_2H_6 was proposed [50], and made these compounds accessible. The novelty in this method was the construction of the reactor, which consisted of two tubes, nesting one within the other. The outer tube is cooled and the inner is heated to the required temperature. The reaction zone is the space between the tubes. This reactor ensures that the removal of the unstable boron hydrides from the reaction zone is as fast as possible. Low-temperature, high-vacuum fractionation [41], or gas chromatography [51] is used to isolate pure B_4H_{10} from the mixture of boron hydrides; the yield of B_4H_{10} reaches 83%. Tetraborane is also formed in the reduction of diboron tetrachloride by metal tetrahydroborates at low temperature [52]:

$$B_2Cl_4 + 4\,LiBH_4 \xrightarrow[-45°]{} B_4H_{10} + B_2H_6 + 4\,LiCl.$$

The reaction is complex, and a mixture of boron hydrides is formed.

Kreyl and Marcus [53] studied the photochemical conversion of B_2H_6 into B_4H_{10} and showed that the mechanism of this reaction is different from the thermal process. The authors think that the reaction proceeds by a free radical path with the intermediate formation of B_2H_5:

$$B_2H_6 + h\nu \rightarrow B_2H_5^{\cdot} + H^{\cdot};\ 2\,B_2H_5^{\cdot} \rightarrow B_4H_{10};\ 2\,H^{\cdot} \rightarrow H_2.$$

An analogous mechanism was proposed for the mercury-sensitised conversion of B_2H_6 into higher boron hydrides [54]. Several patents were taken out on the production of B_4H_{10}:

from B_2H_6 in a silent electric discharge[55] (yield of B_4H_{10} 43–97% in the conversion of 7–36% of the B_2H_6); from B_5H_{11} by its partial hydrolysis at 0°C, 15–50 mmHg pressure, and a time of contact of B_5H_{11} with ice of 1 min.[56,57] The yield of B_4H_{10} reaches 95%.

3. Physical and Chemical Properties of Tetraborane

Tetraborane is a mobile liquid, b.p. 18°C, f.p. -120°C, vapour pressure at 0°C 388 mmHg, density 0.56 at -35°C.[41] It exhibited a high toxicity[58]. As Stock showed[41], B_4H_{10} is unstable at room temperature and slowly breaks down into B_2H_6, B_5H_9, H_2, and involatile boron hydrides. A prolonged experiment, which lasted 340 h,[41] in which B_4H_{10} was put in the cell of an infrared spectrograph at 20° and its infrared spectrum periodically recorded showed that equilibrium is reached between B_4H_{10} and its decomposition products. Study of the kinetics of the conversion of B_4H_{10} into B_5H_{11} [59,60] showed that the reaction proceeds in two stages, the first of which determines the rate of the process:

$$1)\ B_4H_{10} \rightleftarrows B_4H_8 + H_2; \quad 2)\ B_4H_8 + B_2H_6 \rightarrow B_5H_{11} + BH_3.$$

The conversion of B_4H_{10} into B_5H_{11} depends only on the B_4H_{10} concentration; the activation energy of the reaction is 23.4 kcal mole^{-1}. Proof of this course of the reaction is provided by the formation of B_4H_8CO from a mixture of B_4H_{10} and CO in the temperature range 80–110°C.[60] Mass-spectrometric study of the pyrolysis of B_4H_{10} showed[61] that the radicals BH_2 and BH_3 are formed.

In studying the kinetics of deuterium exchange between B_2D_6 and B_4H_{10} at 25–45°C it was found[62] that the exchange can proceed by two different paths. In the first reaction, which has the greater rate at this temperature, two hydrogen atoms are exchanged, with formation of $B_4H_8D_2$; the activation energy is 25.5 kcal mole^{-1}. The exchange is explained by a series of bimolecular reactions in which two hydrogens in the B_4H_{10} molecule which have greater reactivity under ordinary conditions are excited. It is suggested[63] that these are the terminal atoms connected with boron atoms 1 and 3. Under the conditions of the experiment apparently B_4H_8 is not formed, as is confirmed by the lower rate of deuterium exchange between B_4H_{10} and D_2 in comparison with the reaction of B_4H_{10} with B_2D_6:

$$B_4H_{10} + B_4H_{10} \rightleftarrows B_4H_{10}^* + B_4H_{10},$$

$$B_4H_{10} + B_2D_6 \rightleftarrows B_4H_{10}^* + B_2D_6,$$

$$B_4H_{10}^* + B_2D_6 \rightleftarrows B_4H_8D_2 + B_2D_4H_2.$$

At higher temperatures[60,64] loss of the two most mobile hydrogen atoms and the formation of B_4H_8 probably takes place.

In the second path[62] of the deuterium exchange between B_4H_{10} and B_2D_6, eight (or all ten) hydrogen atoms are exchanged. The reaction has an activation energy of 14.1 kcal mole^{-1}, and the rate of this reaction is less temperature-dependent than the first type. The rate-determining stage is the reaction of BD_3 with B_4H_{10}:

$$^{10}B_2D_6 \rightleftarrows 2\,^{10}BD_3,$$

$$^{10}BD_3 + B_4H_{10} \rightarrow {}^{10}BD_3B_3H_7 + BH_3,$$

$$BH_3 + {}^{10}BD_3 \rightarrow BH_3{}^{10}BD_3.$$

The exchange of the atoms ^{10}B–^{11}B between $^{10}B_2H_6$ and B_4H_{10} takes place at one-third of the rate of deuterium exchange[62,64]. The presence of this exchange shows the instability of the B_4H_{10} skeleton. The rate-determining stage is the dissociation of B_4H_{10} into BH_3 and B_3H_7.

In the mass-spectrographic study of the fragments obtained in the bombardment of B_4H_{10} and B_4H_8 by fast electrons (energy 70 eV), Fehlner and Koski[63,65] found that the greatest intensity in the mass spectra was possessed by ions arising as a result of the loss of two atoms of hydrogen or deuterium from the tetraborane molecule: a considerable number of metastable ions obtained by loss of three hydrogens or three deuteriums from the tetraborane molecule was also observed. The authors state that two hydrogen atoms bound to the same boron atom (that is, a terminal and a bridge hydrogen) are lost, leading to the formation of a two-centre B–B bond instead of a B–H–B bridging bond and the liberation of a molecule of H_2. The same authors[8] pyrolysed B_2H_6 and B_4H_{10} in the presence of H_2 in a reactor with a pulsating heater, making possible the isolation of unstable intermediates. It was shown that B_4H_{10} is a precursor of B_5H_{11} in the pyrolysis of B_2H_6, and B_4H_8 is an intermediate. The following equations represent the mechanism:

$$B_4H_{10} \rightleftarrows B_4H_8 + H_2, \qquad B_6H_{12} \rightleftarrows B_6H_{10} + H_2,$$

$$B_4H_{10} \rightleftarrows B_3H_7 + BH_3, \qquad n\,B_4H_8 \rightarrow m\,(\text{solid}) + H_2,$$

$$B_4H_8 + B_2H_6 \rightleftarrows B_5H_{11} + BH_3, \qquad B_3H_7 + H_2 \rightleftarrows B_3H_9,$$

$$B_4H_8 + B_2H_6 \rightarrow B_6H_{12} + H_2, \qquad B_3H_9 + B_2H_6 \rightarrow B_5H_9 + 3\,H_2,$$

$$B_5H_{11} \rightleftarrows B_4H_8 + BH_3.$$

B_2H_6, B_5H_9, B_5H_{11}, B_6H_{10}, and higher boron hydrides have been observed in the pyrolysis products. An increase in the hydrogen concentration has been shown to retard the formation of B_4H_8 as the amount of B_5H_{11} then decreases and the amount of B_5H_9 increases. Schaeffer and Tebbe[9] made boron-labile tetraborane containing three ^{10}B atoms and one ^{11}B atom from $^{10}B_3H_8Na$ and $^{11}B_2H_6$, and also $^{10}B_4H_{10}$, and they showed with the aid of ^{11}B-NMR spectra that ^{11}B is present in four (or two) positions of the tetraborane molecule (the triplet in the weak field region in the $^{10}B_3H_7{}^{11}BH_3$ spectrum corresponding to the BH_2 group has a greater intensity than in the $^{10}B_4H_{10}$ spectrum). The reaction is represented by the following equations:

$$Na^{10}B_3H_8 + HCl \rightarrow NaCl + {}^{10}B_3H_9,$$

$$3/2\,{}^{10}B_2H_6 \leftarrow {}^{10}B_3H_9 \rightarrow {}^{10}B_3H_7 + H_2,$$

$${}^{10}B_3H_7 + {}^{11}B_2H_6 \rightarrow {}^{10}B_3{}^{11}BH_{10} + {}^{11}BH_3.$$

This synthesis is the first example of the preparation of a boron hydride with an isotopic boron atom in a definite position and demonstrates the different mobilities of the boron atoms in the B_4H_{10} molecule.

Tetraborane is slowly hydrolysed by water according to the equation[41,66]:

$$B_4H_{10} + 12\,H_2O \rightarrow 4\,H_3BO_3 + 11\,H_2.$$

The hydrolysis is accelerated on heating or stirring the mixture; the slowness of the hydrolysis is explained by the poor solubility of B_4H_{10} in water. Hydrolysis by dilute acids follows an analogous path. B_4H_9Cl is formed by the action of dry HCl on B_4H_{10}:[66]

$$B_4H_{10} + HCl \rightarrow B_4H_9Cl + H_2.$$

The reaction at room temperature is very slow even in the presence of $AlCl_3$. The reaction product is unstable and breaks down into B_4H_{10} and BCl_3. B_4H_{10} is decomposed

by HCl at 50°C. Reaction of alkali metal amalgams with an excess of B_4H_{10} at 170°C leads to the formation of salts of B_4H_{10} of the composition $K_2B_4H_6$ (or $Na_2B_4H_6$) and the release of hydrogen[67]; on further heating, the mixture gives off hydrogen and $M_2B_4H_6$ and $M_2B_4H_4$ are formed. Under the action of HCl, H is replaced by Cl in the salt[67]. The reaction of NaCN with B_4H_{10} [68] leads to splitting of the latter and the formation of salts with mixed anions:

$$B_4H_{10} + \xrightarrow{NaCN} NaB_3H_7CN + NaB_2H_6CN.$$

In reaction with C_2H_5OH at -78°C, tetraborane is partly (13%) converted into a colourless polymer containing ethoxy--groups but forms mainly $HB(OC_2H_5)_2$ and $B(OC_2H_5)_3$, and also traces of B_2H_6; during the course of the reaction an equimolecular amount of hydrogen is liberated[25]. Shapiro and Weiss[69] studied the alcoholysis of B_4H_{10} by deuterated ethanol at 20°C and showed that the reaction is somewhat different from that for B_2H_6 on account of the presence of B–B bonds. The intermediates in the reaction are $DB(OC_2H_5)_2$ and $HB(OC_2H_5)_2$, that is, the B–B bonds are destroyed simultaneously with the breaking of the B–H bonds. The final product of the reaction is $B(OC_2H_5)_3$.

When iodine in methanol acts on B_4H_{10} there is a rapid exothermic decomposition of the latter with release of hydrogen. This reaction has been proposed for the analytical determination of B_4H_{10}:[70]

$$B_4H_{10} + 9\,I_2 + 12\,CH_3OH \rightarrow 4\,B(OCH_3)_3 + 18\,HI + 2\,H_2.$$

In addition to the above reactions of B_4H_{10}, leading to breakdown of its molecule, it has characteristic reactions in which there is "symmetrical" double bridge splitting, leading to formation of BH_3 and B_3H_7, and "unsymmetrical" double bridge splitting in which BH_2^+ and $B_3H_8^-$ ions are formed. Both these reactions occur when bases act on B_4H_{10}. Fig. 6 shows the decomposition schemes and also the "symmetrical" decomposition of the B_2H_6 molecule for comparison.

Most Lewis bases bring about the symmetrical breakdown of B_4H_{10};[23,25,26,71] this shows a similarity between tetraborane and diborane chemistries.

On treating B_4H_{10} with ethers, amines, or organic sulphides, $B_3H_7.L$ complexes are formed:

$$B_4H_{10} + THF \rightarrow B_3H_7 \cdot C_4H_8O + {}^1/_2\,B_2H_6,$$

$$B_4H_{10} + 2(CH_3)_3N \rightarrow B_3H_7 \cdot (CH_3)_3N + BH_3 \cdot (CH_3)_3N.$$

A second product of the reaction is B_2H_6 or the complex BH_3L, depending on the coordination capacity of the base; the stability of the complex B_3H_7L which is formed also depends on this[26]. As symmetrical decomposition of B_3H_7L also takes place in the presence of an excess of the amine, the reaction of B_4H_{10} under these conditions is by the equation[25]:

$$B_4H_{10} + (3+x)(CH_3)_3N \rightarrow 3(CH_3)_3N \cdot BH_3 + BH[(CH_3)_3N]_x.$$

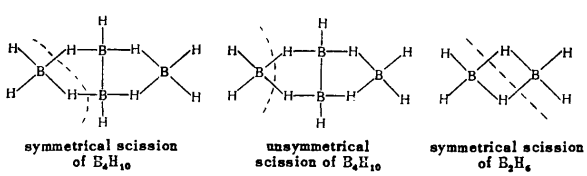


Fig. 6.

An excess of B_4H_{10} decomposes the complex B_3H_7L into B_2H_6, B_5H_9, and H_2.

The reaction of tetraborane with NH_3 follows the path of "unsymmetrical" splitting of the molecule. Stock[66,72] has shown the formation of two unstable compounds of tetraborane with ammonia, $4NH_3.B_4H_{10}$ and $2.5NH_3.B_4H_{10}$. On repeating and studying in greater detail the reaction of B_4H_{10} with NH_3 under various conditions, Kodama and Parry[20,73] established that the substances obtained by Stock are not individual compounds, but a mixture of several. They isolated in the pure state a new compound, "diammoniate of tetraborane" as a stable, white, finely crystalline powder and studied its physical and some of its chemical properties:

$$B_4H_{10} + 2\,NH_3 \xrightarrow[-78°]{(C_2H_5)_2O} B_4H_{10} \cdot 2\,NH_3.$$

A necessary condition for obtaining "diammoniate of tetraborane" is a low temperature and the constant presence of an excess of B_4H_{10}. On the basis of the chemical reactions, an ionic structure was advanced for the compound, $[H_2B(NH_3)_2]^+ . [B_3H_8]^-$, confirmed by the results of X-ray diffraction[16]. It reacts with sodium by the equation:

$$[H_2B(NH_3)_2]^+[B_3H_8]^- + Na \xrightarrow[-78°]{NH_3} NaB_3H_8 + H_2BNH_2 + NH_3 + {}^1/_2\,H_2$$

In this, NaB_3H_8 is obtained in 60–70% yield. This reaction reveals the structure of the anion. Proof of the structure of the cation is provided by reaction with HCl, as a result of which diammineboronium chloride and triborane(7)–ether were produced:

$$[H_2B(NH_3)_2]^+[B_3H_8]^- + HCl \xrightarrow[-78°]{(C_2H_5)_2O} [H_2B(NH_3)_2]Cl + B_3H_7 \cdot O(C_2H_5)_2 + H_2.$$

It was also established that the compounds $6NH_3.B_4H_{10}$ and $7NH_3.B_4H_{10}$ are formed in the prolonged reaction of tetraborane with an excess of NH_3 at -78°C without a solvent[20]. It was shown that in the reaction of NH_3 with B_4H_{10} the solvent plays an important part. When a solvent with considerable coordination capacity (THF, THP) is used there is symmetrical splitting of B_4H_{10} and $B_3H_7.NH_3$ is formed, whereas when a weak Lewis base is used as solvent – $(C_2H_5)_2O$, which does not react with B_4H_{10} at a low temperature (-78°C) – unsymmetrical decomposition of the molecule under the action of ammonia takes place. In these reactions there is an analogy between the chemistries of B_4H_{10} and B_2H_6.

An interesting reaction, leading to greater complexity in the skeleton of the B_4H_{10} molecule, was discovered by Boone and Burg[57]. In the action on B_4H_{10} of bis(dimethylamino)borane at -78°C an addition product of empirical formula $[(CH_3)_2N]_2BH.B_4H_{10}$ is formed, which on heating to -15°C decomposes with formation of B_5H_9, B_4H_{10}, B_2H_6, $[(CH_3)_2N]_2BH$, and $(CH_3)_2NBH_2$. The reaction of B_4H_{10} with 1,2-dimethyldiborane(6) gives a derivative of B_5H_{11}:[74]

$$B_4H_{10} + {}^1/_2(BH_2CH_3)_2 \rightleftarrows B_5H_{10}CH_3 + H_2.$$

The next type of B_4H_{10} reactions are those in which hydrogen atoms are replaced without decomposition of the skeleton of the molecule. $B_4H_9CH_3$ is obtained by the action of $CH_3B_2H_5$ on B_4H_{10}:[74]

$$B_4H_{10} + B_2H_5CH_3 \overset{45°}{\rightleftarrows} B_4H_9CH_3 + B_2H_6,$$

which was identified and characterised by the aid of infrared, NMR, and mass spectra. The infrared spectrum of $B_4H_9CH_3$ shows the asymmetry of the molecule: the principal changes are found in that part of the spectrum which characterises the vibrations of the BH_2B group; therefore the authors think that a hydrogen atom connected with a type II boron atom is replaced.

Harrison and coworkers[75] first studied the reaction of boron hydrides with unsaturated hydrocarbons in the reaction of ethylene with B_4H_{10} in the presence of aluminium chloride. They showed that here also there is replacement of the terminal B–H bonds in the BH_2 group by B–C bonds, with the formation of dimethyltetraborane (70%). The compound is more stable than B_4H_{10}:

$$B_4H_{10} + C_2H_4 \rightarrow B_4H_8C_2H_4 + H_2.$$

The infrared spectrum shows the absence of a BH_2 group and the presence of two types of B–H bonds. The authors consider that the compound has a cyclic bridging structure of unique type, unknown earlier (Fig. 7). The NMR spectra show[76] that the replacement of hydrogen atoms takes place at boron atoms 2 and 4.

The chemical properties of the compound (hydrolysis and alcoholysis) are consistent with the proposed structure[75].

Tetraborane(8)–carbonyl is a very interesting derivative of tetraborane; it was first prepared by Burg and Spielman[77] by the reaction of B_5H_{11} with carbon monoxide in a sealed ampoule at room temperature; later it was obtained[60] by heating B_4H_{10} in the presence of an excess of carbon monoxide at 80–100°C. It is an unstable liquid, which decomposes at room temperature, with liberation of carbon monoxide and higher boron hydrides, and which ignites spontaneously in air (m.p. -114°C, vapour pressure 71.2 mmHg at 0°C, b.p. 59.6°C [77]). A detailed description of the preparation of B_4H_8CO from B_4H_{10} or B_5H_{11} and CO and of its physical and chemical properties has been published[78,79]. Spectroscopic methods were used to establish its structure. The infrared spectrum shows that the molecule contains BH_2 groups, and that the B–CO bond is similar to the bond in BH_3–CO; the infrared spectrum and Raman spectrum of B_4H_8CO differ considerably from those of B_4H_{10}.[79,80] The ^{11}B-NMR spectrum of B_4H_8CO [77,79] contains a doublet in the strong field region typical of the B–H group, and a non-symmetrical triplet in the weak region, which can be ascribed to the BH_2 group. The asymmetry of the triplet is ascribed[78] to the tautomerism of the hydrogen atoms of the B–H–B bridge and terminal B–H bonds (there is a similar tautomerism in the B_5H_{11} molecule)[81]. The structure and the mechanism of formation of B_4H_8CO were not established unambiguously but it was suggested that the most probable place for the addition of CO to the B_4H_8 residue is the boron atom corresponding to the apex in B_5H_{11}, or type I in B_4H_{10}.[73] The most probable structure has the boron atoms at the corners of a trigonal pyramid; the apical boron atom is probably connected by two-centre bonds with two boron atoms of the base, to one of which the CO group is attached; the apical atom is connected with the third boron atom of the base through bridges, similar to the unique bridge in B_5H_{11}. One of the structures proposed for B_4H_8CO is shown in Fig. 8.

The chemical reactions of B_4H_8CO are characterised by rapid but incomplete loss of carbon monoxide and by strong

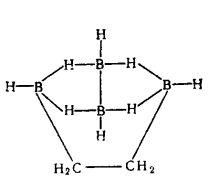


Fig. 7.

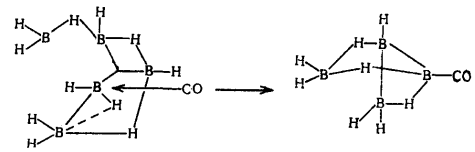


Fig. 8

electron-acceptor properties of the B_4H_8 group[78]. B_4H_8CO has two decomposition paths:

$$B_4H_8CO \rightarrow B_4H_8 + CO, \quad (1)$$

$$B_4H_8CO \rightarrow BH_3 + B_3H_5CO. \quad (2)$$

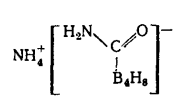
The first path is shown by the formation of B_4H_{10} in the presence of hydrogen or B_5H_{11} in the presence of B_2H_6, the second by the fact that when heated in a vacuum B_4H_8CO does not liberate carbon monoxide, but forms a high-molecular-weight substance containing boron and carbon monoxide[78].

The reactions of B_4H_8CO with electron-donor compounds – $(CH_3)_3N$, C_2H_4, and $(C_2H_5)_2O$ – have been studied[78] and it has been shown that B_4H_8CO exhibits a tendency towards hydrogen replacement reactions; the B–CO bond is rather stable. The reaction with ethylene is most unambiguous:

$$B_4H_8CO + 4\,C_2H_4 \rightarrow (C_2H_5)_4B_4H_4CO.$$

Water hydrolyses B_4H_8CO, but not quantitatively; the residue, which contains B–B bonds, has not been identified.

Parry and coworkers[82] have shown that B_4H_8CO reacts with an excess of ammonia at a low temperature (from -95° to -50°C) to form a compound of composition $B_4H_8CO.2NH_3$, to which, on the basis of its chemical reactions, infrared spectra (the presence of N–H and B–H bonds and of an amide CO bond), and also by analogy with the structure of $BH_3CO.2NH_3$ (studied by the same authors), was ascribed an ionic structure with an anion analogous to carbamate (if it is assumed that the B_4H_8 group is isoelectronic with oxygen):



The following reactions are proof of such a structure:

$$NH_4^+[B_4H_8CONH_2]^- + Na \xrightarrow[-78°]{\text{liq. } NH_3} Na^+[B_4H_8CONH_2]^- + {}^1/_2H_2, \quad (1)$$

$$NH_4^+[B_4H_8CONH_2]^- + LiBH_4 \xrightarrow[14\text{ h}]{\text{THF}} H_3NBH_3 + Li^+[B_4H_8CONH_2]^- + {}^1/_2H_2, \quad (2)$$

and the structure of the cation:

$$NH_4^+[B_4H_8CONH_2]^- + NaB(C_6H_5)_4 \xrightarrow[0°,\ 15\text{ m}]{H_2O} NH_4B(C_6H_5)_4\downarrow + Na^+[B_4H_8CONH_2]^-. \quad (3)$$

The precise structure of the anion $[B_4H_8CONH_2]$ has not been explained; two more probable variants have been proposed. The CO group in B_4H_8CO is readily replaced by PF_3 reversibly[78]:

$$B_4H_8CO + PF_3 \rightleftarrows B_4H_8 \cdot PF_3 + CO.$$

It was shown that when $F_2PN(CH_3)_2$ reacts with B_4H_8CO at -20°C, replacement of CO again takes place readily:

$$B_4H_8CO + F_2PN(CH_3)_2 \rightarrow (CH_3)_2NPF_2 \cdot B_4H_8 + CO.$$

In this compound B_4H_8 is coordinated with a phosphorus atom (P–B bond in the ^{34}P–NMR spectrum). The infrared spectrum is similar to the infrared spectrum of B_4H_8CO.[83]

When B_4H_8CO reacts with an excess of a strong Lewis base — $(CH_3)_3N$ or PF_3 — initially CO is replaced by H, and then B_4H_8 is destroyed and $(CH_3)_3N.BH_3$ or $PF_3.BH_3$ is formed [83,84].

V. PENTABORANE(9)

1. Structure of Pentaborane(9)

Pentaborane(9) is one of the most studied boron hydrides and the geometry of its molecule has been accurately determined by several physical methods, which give concordant results: X-ray diffraction [85,86], electron diffraction [87], and microwave spectroscopy [88]. All these results suggest that the B_5H_9 molecule has the structure shown in Fig. 9.

The most accurate data on the interatomic distances in B_5H_9, obtained from the microwave spectra [88], are: $B_{(1)}-B_{(3)} = 1.687 \pm 0.005$ Å; $B_{(3)}-B_{(4)} = 1.800 \pm 0.003$ Å; $B-H_{terminal} = 1.22 \pm 0.04$ Å; $B_{(2)}-H_{bridge} = B_{(3)}-H_{bridge} = 1.35 \pm 0.02$ Å; $\angle B_{(1)}B_{(2)}H_{(2)} = 136° 10' \pm 30'$; angle between planes $B_{(1)}B_{(2)}B_{(3)}$ and $B_{(2)}B_{(3)}H_{bridge} = 196° \pm 2°$. X-Ray diffraction [85,86] showed that B_5H_9 crystals have C_{4v} symmetry and contain two molecules in the unit cell with parameters $a = 7.16$, $c = 5.38$ Å.

On the basis of the geometry of the molecules Lipscomb and coworkers [11] proposed a structure for B_5H_9 in which the five boron atoms form a tetragonal pyramid, which is a fragment of an octahedron. Each boron atom in the base of the pyramid (type *II* in Fig. 9) forms one terminal B–H bond and two B–H–B bridging bonds. Three sp^3-orbitals and two electrons of the base boron atoms are used in these bonds; the remaining sp^3-orbital and electron of each B_{II} atom is used for a bond with an apical boron atom (type *I* in Fig. 9), which forms one terminal B–H bond directed along the axis of symmetry of the molecule. The remaining three orbitals and two electrons of the apical boron atom are used for bonds with the basal boron atoms. It is assumed that one of these orbitals has sp-hybridisation and is directed along the axis of symmetry towards the centre of the molecule; two other orbitals are "pure" p-orbitals directed perpendicularly to the symmetry axis, one of them being situated in the $B_{(2)}-B_{(1)}-B_{(4)}$ plane and directed towards $B_{(4)}$, and the other being in the $B_{(3)}-B_{(1)}-B_{(5)}$ plane and directed towards $B_{(3)}$. Rather later Lipscomb [10,89] and also Moore [90], in calculating the molecular orbitals of B_5H_9 and their overlap integrals, concluded that the apical atom $B_{(1)}$ forms two two-centre bonds with two of the boron atoms of the base and one open three-centre bond with the other two boron atoms of the base, using in this all the remaining six electrons and seven orbitals of the boron atoms. As in this the molecule does not have C_{4v} symmetry; the authors assume that here it is possible to write two equivalent structural formulae (as in the C_6H_6 molecule) in which the open three-centre $B_{II}-B_I-B_{II}$ bond and two two-centre B_I-B_{II} bonds exchange places. Moore [90] also calculated the formal charges of the boron atoms ($B_I = -0.870$ e, $B_{II} = +0.217$ e) and from these results obtained a calculated value of the dipole moment of $B_5H_9 = 1.7-2.0$ D (with allowance for the hydride character of the bridge hydrogen atoms, -0.2 e, and apical hydrogen atom, -0.1 e). This agrees with the experimental value, 2.13 ± 0.04 D. [88]

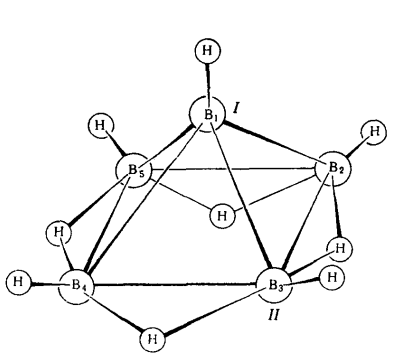


Fig. 9.

The ^{11}B-NMR spectrum of B_5H_9 [91] shows that the molecule has four identical boron atoms (each of which is connected with one terminal hydrogen atom) and one boron atom having resonance in the region of higher field, that is, more negative, also connected with one hydrogen atom (two doublets with ratio of peak intensities 4 : 4 : 1 : 1). These results agree with the structure proposed for B_5H_9. The ^1H-NMR spectrum of B_5H_9, [91,92] obtained by use of the technique of "spin saturation" of ^{11}B nuclei, suggests that the terminal hydrogen atom of the apical boron atom is somewhat more negative than the terminal hydrogens on the basal boron atoms, but less negative than the bridge hydrogen atoms.

On the basis of the experimental results on the geometry of the molecule [85,87] Glockler [93] calculated the energies of the bonds in B_5H_9. The heat of formation obtained from the calculated data ($\Delta Ha_\circ = 1146.7$ kcal mole^{-1}) is considerably different from that determined experimentally (1092.73 kcal mole^{-1}).

2. Preparation of Pentaborane(9)

B_5H_9 is present in small amounts in the gas mixture obtained on decomposing metal borides with acids. Stock and Kuss first isolated pentaborane(9) from this mixture [94] but the yield of B_5H_9 in this is extremely small (< 1%), and the compound is contaminated with other boron hydrides, particularly B_5H_{11}, from which B_5H_9 is difficult to separate owing to their similar boiling points (the difference in b.p. at 100 mmHg is 4 deg). Therefore B_5H_9 was an almost inaccessible compound until Schlesinger and Burg [46] obtained it in 1931 in 20% yield by heating B_2H_6 at 120–130° with a little dry HCl or BCl_3. Somewhat later the same authors [47] increased the yield of B_5H_9 to 33%. Then Stock found [48] that a mixture of B_5H_9 (54–56%) and B_5H_{11} (10–26%) is formed in the pyrolysis of diborane over mercury at 250–300° or tetraborane at 100–200°.

A detailed study was made [95] of the kinetics of pyrolysis of B_2H_6 in the temperature range 80–120°, by three methods: (1) from the rate of increase of the total pressure in the system; (2) from the rate of formation of H_2, and (3) mass spectrometrically. The following conclusions were drawn: (1) the reaction products are H_2, B_4H_{10}, B_5H_{11}, B_5H_9, and higher boron hydrides; (2) the process has a complex path; (3) B_5H_{11} is an intermediate in the formation of most other boron hydrides from B_2H_6; (4) the formation of B_5H_9 from B_5H_{11} is a first-order reaction. It was suggested [96] that the rate-determining stage of the pyrolysis of B_2H_6 is the reaction:

$$B_5H_{11}+H_2 \rightleftarrows B_4H_{10}+\tfrac{1}{2}B_2H_6.$$

The B_4H_{10} formed reacts with B_5H_{11}:

$$B_4H_{10} + B_5H_{11} \rightarrow B_5H_9 + 2B_2H_6.$$

These two stages were proposed to explain the conversion of B_5H_{11} into B_5H_9. Fehlner and Koski[8] showed, by pulsation heating of B_2H_6, that the reaction products are H_2, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, B_7H_{11}, B_7H_{13}, and higher boron hydrides. Using isotopic labelling, and on the basis of the composition of the intermediate and final products of the reaction, the authors established the mechanism of the pyrolysis of diborane, which includes a series of competing reactions and equilibria. It was shown that the formation of B_5H_9 proceeds along a path different from the formation of B_4H_{10} and B_6H_{10}, namely through the formation of triborane by the reactions:

$$B_2H_6 \rightleftarrows 2BH_3,$$

$$BH_3 + B_2H_6 \rightarrow B_3H_9,$$

$$B_3H_9 + B_2H_6 \rightarrow B_5H_9 + 3H_2.$$

Confirmation is given by the fact that in the pyrolysis of B_4H_{10} in the presence of hydrogen raising the concentration of the latter increases the degree of conversion of B_4H_{10} into B_5H_9, which also proceeds through the formation of B_3H_9:

$$B_4H_{10} \rightleftarrows B_3H_7 + BH_3,$$

$$B_3H_7 + H_2 \rightleftarrows B_3H_9,$$

$$B_3H_9 + B_2H_6 \rightarrow B_5H_9 + 3H_2.$$

With the aim of finding the most favourable conditions for the conversion of B_2H_6 into B_5H_9, McCarty and Di Giorgio[97] studied the effect of temperature (in the range 175–250°), additions of hydrogen and nitrogen, and time on the reaction; they showed that the pyrolysis of diborane is exothermic and that varying the conditions makes possible the direction of the process towards the boron hydride required. Conditions were found under which B_5H_9 is obtained without B_5H_{11} as impurity, which removed one of the main disadvantages of this method of making B_5H_9 — previously the B_5H_9 was freed from B_5H_{11} by either further heating of the mixture until the B_5H_{11} had decomposed, or contacting the mixture at 0°C with Lewis bases and then distilling off the pure B_5H_9; during this the loss of pentaborane(9) was considerable. On the basis of this work[97] and that of Bragg and coworkers[95] a method for the industrial production of B_5H_9 was developed[98]. The overall pyrolysis of diborane is represented by the following schemes:

$$5B_2H_6 \rightarrow 2B_5H_9 + 6H_2, \quad (1)$$

$$5B_2H_6 \rightarrow B_{10}H_{14} + 8H_2, \quad (2)$$

$$B_2H_6 \rightarrow (BH)_x(\text{solid}) + H_2. \quad (3)$$

Of the B_2H_6 taken 70–85% decomposes by reactions (1) and (2); the residue consists of high-molecular-weight boron hydride of unknown composition. The conditions for obtaining B_5H_9 are: temperature of the reaction zone 240–290°C, pressure ~3.5 atm, time of B_2H_6 at this temperature 3 s (then the reaction gases are cooled to 35°C), and an equimolecular quantity of hydrogen is used as the reaction medium. Not less than 80% of the B_2H_6 enters into the reaction and the yield of pure B_5H_9 is 38% (purity 99.9%).

Jeffers[99] has proposed a convenient path for the preparation of pentaborane(9): pyrolysis of diborane by the method of hot (200°C) and cold (-90°C) tubes; the yield of B_5H_9 is 60% at a 90% conversion of B_2H_6.

A patent has been taken out[100] for preparing B_5H_9 by a similar method: hot zone temperature 205°C, cold -40°C, contact time 2 s, yield 80%.

3. Physical Properties of Pentaborane(9)

B_5H_9 is a colourless mobile liquid with an unpleasant odour, b.p. 58°C [41] or 60.0°C,[101] m.p. -46.6°C [41] or 226.41° ± 0.02°K.[102] Several values are given for the density of B_5H_9 at 0°C: 0.61 g ml^{-1},[41] 0.642 g cm^{-3},[103] 0.637 ± ± 0.002 g ml^{-1};[104] the last two results are evidently the most accurate; the temperature dependence of the density of B_5H_9 is $d = 0.8674 - 0.00082T$.[103] The vapour pressure of B_5H_9 at 0°C is 66 mmHg;[41] according to more recent data[102] $P_{B_5H_9} = 64.77$ mmHg at 272.99°K; the variation of the vapour pressure of B_5H_9 with temperature in the range 226–298°K is described by the equation.

$$\log p_{\text{mmHg}} = 9.96491 - \frac{1951 \times 14}{T} - 0.0036884T.$$

The viscosity of B_5H_9 at 274.1°K has been measured (η = 3.94 mP), as has the surface tension at 269.5°K (γ = 24.5 dyn cm^{-1}) and 286.2°K (γ = 22.0 dyn cm^{-1}).[103] The electrical properties of B_5H_9 have been measured[102] and it has been shown that liquid B_5H_9 has a high dielectric constant, which varies between the limits 21.1 (298°K) and 53.1 (at the melting point, 226.41°K). The apparent dipole moment of B_5H_9 varies from 3.37 D at 298°K to 4.54 D at the melting point, and in the gas phase the dipole moment is 2.13 D, that is, pentaborane(9) is a highly polar substance[102]. The value of 2.13 D for B_5H_9 has been given elsewhere[88]. Crystals of B_5H_9 have two modifications[102]: the body-centred tetragonal crystals are converted into simple tetragonal crystals in the range 130–140°K. The heat of formation of gaseous B_5H_9 from the elements[105] is 12.99 ± 0.39 kcal mole^{-1} and its entropy[106] is 65.75 cal × × deg^{-1} mole^{-1}.

Pentaborane(9) is a highly poisonous compound[107], more toxic than diborane or decaborane. Systematic inhalation of B_5H_9 at a concentration of 0.2 parts per million by various animals leads to loss of appetite and weight, apathy, and a drop in physical and mental activity.

4. Chemical Properties of Pentaborane(9)

(a) Stability of pentaborane(9). The mass-spectrometric investigation of pentaborane(9) and deuteriopentaborane(9) [101] shows a clear tendency for these molecules to lose two or four hydrogen (or deuterium) atoms, and a much smaller tendency to lose one or three hydrogen atoms. Starting from the values of the energies of the terminal B–H and bridge B–H–B bonds (4.04 and 4.66 eV respectively) Kaufman and coworkers[108] gave reasons why, in the attack of fast electrons of 70 eV energy, the terminal B–H bonds in the B_5H_9 molecule are broken more readily, and then the molecule is reconstituted: probably a three-centre B–H–B bond is changed into B–H and B–B two-centre bonds. However, the precise path for the reconstitution of the molecule during the formation of fragment ions has not been established[65]. The authors determined the potentials for the appearance of $^{11}B_5H_9^+$ and $^{11}B_5D_9^+$, 10.39 and 9.78 eV respectively. Previously[109] the ionisation potential of B_5H_9 had been given as I = 10.8 ± 0.5 eV.

When an electric discharge acts on B_5H_9 [110] a terminal B–H bond at the apical boron atom is broken and a B_5H_8 radical is formed, which combines with a second such radical to form a $B_{10}H_{16}$ molecule. As Hall and Koski have shown[111], an analogous reaction occurs when B_5H_9 is irradiated with deuterons of 2 MeV energy. These authors

established[112] that the products of the reaction are H_2, B_2H_6, $B_{10}H_{16}$, and polymeric boron hydrides; B_5H_9 undergoes 5% decomposition. The radiochemical yields of the products were found to be: $G_{H_2} = 13.1$, $G_{B_2H_6} = 1.7$, $G_{B_{10}H_{16}} = 0.8$ mole per 100 eV. A radical mechanism for the reaction was proposed, based on experiments using D_2 as indicator, inert gases (He, Ne, Ar) as sensitisers, and I_2 as an inhibitor of the process.

NMR spectra showed[113] that in the reaction of B_5H_9 with B_2D_6 only terminal hydrogen atoms are replaced by deuterons, the bridge hydrogens not taking part in the exchange reaction. The rate of exchange of the apical hydrogen atom in this was the same as that of the terminal basal hydrogen atoms (within the limits of experimental error, ±10%). Similar results were obtained in studying deuterium exchange between B_5H_9 and B_2D_6 at 80° without a catalyst, using infrared and mass spectra[114,115].

All the hydrogen atoms are replaced by deuterium in the reaction of B_5H_9 with an excess of deuterium in the presence of a chromium–aluminium dehydrogenation catalyst ($Cr_2O_3.Al_2O_3$) at 20–25°C.[106]

Onak and Williams[116] made a directed deuterium exchange between B_5H_9 and DCl in the presence of $AlCl_3$ at 20°C: only the apical hydrogen atom is exchanged; the compound B_5H_8D which is obtained is rather stable; it is unchanged after heating for 17 h at 105°C. The H–D exchange in the presence of an electrophilic catalyst confirms the greater susceptibility to electrophilic attack of the apical hydrogen atom. The authors showed[117] that intramolecular H–D exchange takes place in the B_5H_8D molecule in the presence of 2,6-dimethylpyridine at 20°C, but without a Lewis base at elevated temperatures (145–200°C) there is intermolecular exchange. In all the reactions mentioned above there is a clear difference in the behaviour of the terminal and bridging hydrogen atoms in the B_5H_9 molecule, and also in that of the apical hydrogen and the basal hydrogen atoms.

The stability of the B_5H_9 molecule was shown by studying the exchange of ^{11}B and ^{10}B atoms: under conditions at which exchange of ^{11}B for ^{10}B takes place in diborane or tetraborane molecules there is no exchange in the pentaborane(9) molecule[118]; reaction between B_5H_9 and $^{10}B_5H_9$ does not take place up to 100°C in the liquid phase or up to 250°C in the gas phase. H–D exchange is observed between B_5H_9 and B_5D_9 at 200°C in the absence of a catalyst. Shapiro and coworkers[119] showed that in the presence of a catalyst (γ-Al_2O_3) at 90°C there is exchange of boron atoms between $^{10}B_2H_6$ and B_5H_9 through the intermediate formation of the complex $Al_2O_3.^{10}B_2H_6$, which then slowly exchanges ^{10}B atoms with the pentaborane. This reaction occurs much more slowly than for B_2H_6.

According to the results of Stock and coworkers[67], pentaborane(9) reacts with alkali metal amalgams like B_4H_{10} and B_2H_6, forming salts of composition $M_2B_5H_9$; they could not be obtained pure. However, Ford and coworkers[120] showed that B_5H_9 does not react with sodium amalgam and sodium hydride in ether at 20–25°C.

(b) Oxidation of pentaborane(9). B_5H_9 ignites spontaneously on mixing with air. The kinetics and mechanism of the oxidation of pentaborane have been studied several times to determine the conditions for the most convenient use of this reaction. A kinetic study of the B_5H_9–O_2 system[121] showed that the lower explosive limit at room temperature is at very low pressures of B_5H_9 and O_2; a B_5H_9 pressure between 1 and 5 mmHg is critical. The reaction proceeds by a type of branched-chain mechanism. Later work[122] confirmed the conclusion about the reaction type. Intermediate products were not isolated, but it was observed that $Fe(CO)_5$ has a strong inhibiting action, showing that oxygen atoms participate in the chain development. The lower explosive limits were determined for B_5H_9–O_2 mixtures at B_5H_9 pressures from 1 to 90 mmHg and temperatures of 15° and 21.5°C, and it was also shown that the final reaction product is H_3BO_3. It was shown[123] that during the slow oxidation of B_5H_9 initially H_2, B_2H_6, and a more solid substance of unknown composition are formed; the formula $B_4H_{12}O$ was proposed for the latter on the basis of its infrared and mass spectra[124]. It was concluded in a more detailed study of the partial oxidation of B_5H_9 by spectrometric methods[125] that the intermediate compound has the formula $B_2H_2O_3$ and a trigonal bipyramidal structure formed by boron and oxygen atoms with a terminal hydrogen atom at each boron. It was shown[126] that during the explosive oxidation of B_5H_9 yet another intermediate product is formed, $B_3O_3H_3$, identical with boroxole[127].

(c) Reaction of pentaborane(9) with oxygen compounds. Pentaborane(9)[41] is slowly hydrolysed by water at room temperature; for complete hydrolysis prolonged heating of it with water at 90°C is necessary. However, in aqueous dioxan solution the reaction is rather rapid and the hydrolysis rate can be measured by the increase in pressure[128]:

$$B_5H_9 + 15\,H_2O \rightarrow 5\,B(OH)_3 + 12\,H_2.$$

The first stage of the hydrolysis was studied by mass spectroscopy[129]; B_5H_9 was hydrolysed by water contained in silica gel in a combined form as OH^- ions. The mass spectrum of the product of the reaction was similar to that of B_4H_{10}. It is assumed that the first stage of the hydrolysis is the displacement by water of a boron atom from the B_5H_9 molecule (probably one of the four basal atoms) with subsequent regeneration of hydrogen. The balance in boron and hydrogen of the reaction products found on the silica gel and in the volatile products confirms this conclusion.

The interaction of B_5H_9 with alcohols[130] leads to the formation of borate esters and hydrogen:

$$B_5H_9 + 15\,ROH \rightarrow 5\,B(OR)_3 + 12\,H_2.$$

When the alcohol is added to B_5H_9 in stoichiometric proportion the borate ester is formed in quantitative yield under mild conditions; the reaction is exothermic. The intermediate product, diethoxyborane $HB(OC_2H_5)_2$, was isolated pure. Alcoholysis of the B–B bond in pentaborane was studied by using deuterated ethanol[69] and compared with the alcoholysis of diborane. It was shown that the course of the alcoholysis with B_5H_9 is different from that for B_2H_6, and similar to the alcoholysis of B_4H_{10}; during the action of alcohol on B_5H_9 there is simultaneous formation of $HB(OC_2H_5)_3$ and $B(OC_2H_5)_3$, that is, the B–B bonds are split simultaneously with the B–H bonds and not subsequently. The relative concentrations of the intermediate products $HB(OC_2H_5)_2$ and $DB(OC_2H_5)_2$ depend on the structures of the boron hydrides (B_4H_{10} and B_5H_9), and thus on the nature and number of the B–B bonds and B–H–B bridge bonds. In the splitting of the B–H–B bond by deuterioethanol only $HB(OC_2H_5)_2$ is formed; in the splitting of the B–B bonds, $DB(OC_2H_5)_2$. Pentaborane(9) reacts exothermically with acetone both at room

temperature and at -80°C.[130] The reaction is complex and the reaction mechanism is still unexplained. Isopropyl borate (25–30% yield) has been separated from the reaction mixture. When dry acetone acts on B_5H_9 hydrogen is not liberated, that is, reaction probably does not occur.

(d) Halogen derivatives of pentaborane(9). Under carefully controlled conditions B_5H_9 reacts with halogens, hydrogen halides, or BCl_3 with replacement of one hydrogen atom by halogen. Schlesinger and Burg[71] obtained B_5H_8Cl by direct chlorination of B_5H_9 at -80°C. B_5H_8Cl, B_5H_8Br, and B_5H_8I were obtained by halogenation of pentaborane(9) in the presence of $AlCl_3$ in a medium of CS_2;[131] during this B_5H_8Br (m.p. 32–34°C) and B_5H_8I (m.p. 53°C) were obtained pure with good yields; B_5H_8Cl could be obtained only in trace amounts (owing to its explosive properties) and contaminated by CCl_4. A patent had been issued earlier[132] on a method of obtaining B_5H_8Br by brominating B_5H_9 under specified conditions (yield 70%, m.p. 34–36°C, b.p. 80–82°/34 mmHg). The precise position of the halogen in the monohalogenopentaborane molecules was established by infrared and NMR spectra. The infrared spectra of B_5H_8Br [133] is similar to the spectrum of B_5H_9; the symmetry of the molecule is retained, which is possible only if the bromine replaces the hydrogen atom of the apical boron atom. The NMR spectrum of B_5H_8X [134] also shows with certainty that the substitution occurs at the apical boron atom; the ^1H–NMR spectra of B_5H_8Br and B_5H_8I contain a doublet of peaks of equal intensity, which show equal numbers of terminal and bridge hydrogen atoms; the ^{11}B-NMR spectra of B_5H_8Br and B_5H_8I do not show the doublet corresponding to the interaction of the apical boron atom with the terminal hydrogen, it being converted into a singlet of double intensity; the doublet corresponding to the basal BH groups is unchanged. The inductive influence of halogens on the ^{11}B-chemical shift in the ^{11}B-NMR spectrum of B_5H_8X (X = Br or I) is observed. The effect of a change in the shift to low field with increase in the electronegativity of the atoms bound to boron has also been shown for other boron compounds[135]. An exchange reaction between the halogen in 1-BrB_5H_8 and chlorine has also been carried out[136], in which the halogen atom is transferred from the apical boron atom to a basal boron atom. The reaction proceeds in the presence of $AlCl_3$ and is the first instance of an exchange of a halogen atom in a higher boron hydride taking place with change in bonding position. The mechanism of the reaction is not clear. Attempts to obtain 2-BrB_5H_8 by the reaction of 1-BrB_5H_8 with $AlBr_3$ or 2-ClB_5H_8 by the reaction of 1-BrB_5H_8 with BCl_3 were unsuccessful.

In a mass spectrometric study of halogenopentaboranes (1-ClB_5H_8, 1-BrB_5H_8, and 1-IB_5H_8) it was found[131] that: (1) the B–I bond is relatively easily broken; (2) the detachment of the Br (or Cl) atom from a B_5H_8X molecule occurs only when the skeleton is destroyed, that is, by loss of a BBr (BCl) group; (3) the general distribution of fragment ions in the mass spectrum of B_5H_8I (and to some extent B_5H_8Br) is similar to that in B_5H_9. From these results a sequence was derived for the relative ease of bond-breaking in the halogenopentaboranes: BI > BH > BB > BBr or BCl.

(e) Reactions of pentaborane(9) with nitrogen and phosphorus compounds. The reaction of B_5H_9 with secondary and tertiary amines has been studied in detail by Zhigach and coworkers[137]. At a low temperature (up to 0°C, usually from -3° to -5°C) B_5H_9 adds secondary amines with formation of complexes of composition $n NHR_2.B_5H_9$ (n = 2, 3, 4, or 5; R = CH_3 or C_2H_5); under the action of tertiary amines the compounds $2NR_3.B_5H_9$ are formed (R = CH_3 or C_2H_5) stable up to 0°C. At elevated temperature (100–120°C) the complexes are completely decomposed with liberation of hydrogen, splitting of the B_5H_9 molecule, and formation of alkylamino-derivatives of diborane and borane and of polymers. An increase in the proportion of amine in the original complex leads to an increase in the amount of borane derivatives and a decrease in the amount of diborane derivatives in its decomposition products.

Burg[138] showed simultaneously that $(CH_3)_3N$ at -78°C adds to B_5H_9 with formation of a complex $2(CH_3)_3N.B_5H_9$, which on heating in a vacuum is partly decomposed to the initial substances and partly converted into $(CH_3)_3N.BH_3$ and a polymer of composition $(BH)_x$. On heating the complex above 100°C with an excess of trimethylamine 2 moles $(CH_3)_3N.BH_3$ are formed per 1 mole B_5H_9 and a polymer which exhibits thermoplastic properties[139].

In the reaction of B_5H_9 with $(CH_3)_2NH$ and also with $(CH_3)_2NBH_2$ or $[(CH_3)_2N]_2BH$ in stoichiometric amount, Burg[138] obtained a compound of low stability in air, which as X-ray analysis showed[140], is a trimer of dimethylaminoborane. Campbell and Johnson[141] came to the same conclusion, in studying the reaction of B_5H_9 with $[(CH_3)_2NBH_2]_2$ and identifying the reaction products by ^1H- and ^{11}B-NMR spectra, analysis, and molecular weight.

Hough and coworkers[142] also studied the reaction of B_5H_9 with $(CH_3)_3N$ and considered that at 20–25°C the reaction proceeds according to the equation:

$$B_5H_9 + (CH_3)_3N \xrightarrow{\text{rapid}} [(CH_3)_3N]_2 \cdot B_5H_9 \xrightarrow{\text{slow}} (CH_3)_3N \cdot BH_3 + (CH_3)_3N \cdot B_4H_8.$$

Under the action of an excess of the amine two moles $(CH_3)_3N.BH_3$ and 1 mole of the polymer $[(CH_3)_3N]_x.(B_3H_3)_x$ are formed per mole B_5H_9.[143] From what has been said above it is evident that the reaction of B_5H_9 with amines is complex with splitting of the B_5H_9 molecule. There has been little investigation of the reaction of pentaborane with ammonia. Schlesinger and Burg[71] state that "tetra-ammoniate of pentaborane" is formed in the reaction of B_5H_9 with NH_3; one of the nitrogens in it is in the form of an ammonium ion: further slow reaction of B_5H_9 with NH_3 leads to the formation of "tetra-ammoniate of pentaborane"; however, it was not found whether this substance was pure.

In Schaeffer's work[144] on the reaction of decaborane with CH_3CN it is stated that B_5H_9 reacts with CH_3CN with liberation of hydrogen and formation of a substitution product. The mixed salt NaB_5H_9CN is formed by the reaction of B_5H_9 with NaCN.[68]

Muetterties and coworkers[145] showed that in the reaction of B_5H_9 with *NNN'N'*-tetramethylethylenediammine (TMED) at 25°C the addition product TMED.B_5H_9 is formed, which under the action of CH_3OH at 0°C is converted into TMED.B_4H_8. The authors consider these two addition products to be derivatives of the hypothetical anions $B_5H_{11}^{-2}$ and $B_4H_{10}^{-2}$.

Burg[139] studied the reaction of B_5H_9 with phosphorus-containing Lewis bases and showed that during this the B_5H_9 molecule is split although with much greater difficulty than for B_4H_{10}. The reaction products are a cyclic trimer of composition $[R_2P-BH_2]_3$ and the tetramer $[R_2P-BH_2]_4$ in small amount and also the extremely stable boron hydride thermoplastic polymers. The polymer is unchanged on heating to 250–300°C and does not liberate H_2, $(CH_3)_3P$, or

$(CH_3)_3P.BH_3$; on heating to 400°C, there is partial liberation of hydrogen and an increase in the B : P ratio. Pentaborane(9) reacts with aminophosphines and diphosphines in a similar manner, during which it also forms the corresponding cyclic trimers and polymers. Jeffers[99] studied the reaction of B_5H_9 with $(CH_3)_3P$ and the pyrolysis of the addition compounds thus formed, as a result of which a polymer with empirical formula $BH(PR_3)_{0.2}$ is obtained. It is assumed that the polymer forms a boron hydride chain of rubber type in which are introduced molecules of the base coordinated to the boron atoms.

(f) Alkylation of pentaborane(9). The alkylation of B_5H_9 has been studied in some detail. The alkylation has been carried out under conditions of electrophilic and nucleophilic reactions using various alkylating agents. The products have been isolated and their structure determined with the aid of chromatography and infrared and NMR spectra.

In electrophilic (Friedel–Crafts) alkylation of B_5H_9 the apical hydrogen, where the charge density is greatest, is replaced. In the nucleophilic attack of alkenes on B_5H_9, the basal hydrogen atoms are replaced.

Williams and coworkers[146] carried out the reaction of ethylene with diborane at 100°C and obtained a complex mixture of products which was separated chromatographically into two homologous series: ethylpentaborane(9)s (mono-, di-, and poly-ethylpentaboranes) and ethyldecaborane(14)s (mono-, di-, and poly-ethyldecaboranes). Evidently under these conditions reaction occurred between the B_5H_9 and $B_{10}H_{14}$ formed from the diborane and the alkylating agents: C_2H_4, ethyldiboranes, and $(C_2H_5)_3B$. It was shown that the basal hydrogen atoms are replaced. Ryschkewitsch and coworkers[147] obtained a series of alkyl derivatives of B_5H_9 by the reaction of alkenes (but-1-ene, 2-methylprop--1-ene, but-2-ene, ethylene) with pentaborane(9) at 150°C. Replacement also took place at the basal boron atoms; alkenes apparently directly attack the B_5H_9 molecule at the points of least electron density. The absence of isomeric alkyl radicals attached to the boron hydride is explained by the alkene molecule's adding to the B_5H_9 at the carbon atom having the highest electron density. The reactivity of the alkenes increases in the sequence:

$$C_2H_4 < CH_2{=}CH{-}CH_2CH_3 < CH_3CH{=}CHCH_3 \leqslant CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_3.$$

The ^{11}B-NMR spectra of RB_5H_8 contain two doublets, which shows the presence of a hydrogen atom at the apical boron. The alkylpentaboranes obtained[147] are colourless mobile liquids with a characteristic odour; in a homogeneous mixture with water they are rapidly hydrolysed; in contact with pure water they are hydrolysed slowly owing to the low solubility; they are rapidly oxidised in air and are capable of spontaneous ignition; they slowly decompose when heated in a vacuum to 150°C; they react with aliphatic amines like B_5H_9.

When pentaborane reacts with ethylene under conditions of electrophilic substitution in the presence of $AlCl_3$, ethylpentaborane is obtained[133,148]; it was shown chromatographically and with the aid of infrared and NMR spectra that under these conditions only the apical hydrogen atom is replaced. Similar results were obtained in the alkylation of B_5H_9 at 100°C by methyl chloride or ethylene in the presence of $AlCl_3$;[149] $1\text{-}CH_3B_5H_8$ is obtained in 80% yield and $1\text{-}C_2H_5B_5H_8$ in 50% yield. It was proposed[150] to use the reaction of alkenes or alkyl halides with pentaborane in the presence of $AlCl_3$, $FeCl_3$, or $SnCl_4$ as a general method for making alkylpentaboranes with an apical alkyl radical. In this way the following compounds were prepared and characterised: 1-methylpentaborane, 1-ethylpentaborane, 1-isopropylpentaborane, 1-s-butylpentaborane, and also a disubstituted product: 2-s-butyl-1-methylpentaborane. The production of a disubstituted pentaborane shows that the alkylation does not deactivate the B_5H_9 molecule in relation to further catalytic alkylation. Apical-substituted B_5H_8R derivatives are thermodynamically less stable than those substituted at a basal boron atom by 3 kcal $mole^{-1}$; therefore the direction of the substitution is determined by the mechanism of the reaction and not by the thermodynamic stability of the compounds. 1-Alkylpentaboranes are very sensitive to oxidation and hydrolysis and do not react with anhydrous HCl, but are decomposed by HCl in the presence of $AlCl_3$.

A series of patents have been taken out on methods for making alkylpentaboranes, and can be classified as follows:

1. Reaction of B_5H_9 with an alkene in the presence of catalysts — Lewis acids ($AlCl_3$, $FeCl_3$, $AlBr_3$),[151,152] the yield of 1-alkylpentaboranes being 65–68%.
2. The reaction of B_5H_9 with an alkene in the presence of basic catalysts (pyridine and alkylpyridines[153], yield of $t\text{-}C_4H_9B_5H_8$ 40.4%; tetrahydrofuran[154]; lower alkylamines[155], yield of $t\text{-}C_4H_9B_5H_8$ 43%).
3. Reaction of B_5H_9 with alkyl monohalides using Friedel–Crafts catalysts, the yield of 1-alkylpentaboranes being 80–90%.[156,157]
4. Alkyl borates, alkyl silicates, diethylborane, alkyl ester–BF_3 adducts are used as alkylating agents in the reaction with B_5H_9.[158-160]

To free alkylpentaboranes from impurities they are heated with metal oxides, the best being Fe_2O_3 or Al_2O_3.[161]

In 1961 Onak[162] observed that 1-alkylpentaborane(9) (R = CH_3 or C_2H_5) is quantitatively converted into 2-alkylpentaborane(9) in the presence of 2,6-dimethylpyridine at room temperature. The structure of the initial and final products was shown by infrared and ^{11}B-NMR spectra. The analogous conversion of 1-ethylpentaborane, obtained from B_5H_9 and C_2H_4 in the presence of $AlCl_3$, into its isomer takes place on heating to 200°C [149] but ethylpentaboranes of a higher degree of alkylation are not obtained. This rearrangement is explained by the greater thermodynamic stability of basal-substituted alkylpentaborane[150]. Hough and coworkers[163] studied such a rearrangement of $1\text{-}C_2H_5B_5H_8$ into $2\text{-}C_2H_5B_5H_8$ in the presence of $(CH_3)_3N$ at 27–28°C. Rearrangement takes place in the presence of Lewis bases (2,6-dimethylpyridine or trimethylamine), probably by intramolecular exchange of alkyl groups facilitated by the formation of an addition product of alkylpentaborane with the base. Such an addition product, $[(CH_3)_3NHB_5H_7C_2H_5]$, formed from $1\text{-}C_2H_5B_5H_8$ and $(CH_3)_3N$, was isolated at a low temperature[163]; it dissociates at 27–28°C, that is, at the temperature of formation of $2\text{-}C_2H_5B_5H_8$. To explain the mechanism of the rearrangement allowance must also be made for the recurrence of the intramolecular hydrogen exchange in B_5H_9 (as in the other boron hydrides), shown by Williams[17,81]. Onak and coworkers[117] showed that in the presence of 2,6-dimethylpyridine an intramolecular exchange takes place in 1-deuteriopentaborane(9) and intermolecular exchange does not occur; at elevated temperatures (above 145°C) exchange of H for D takes place by an

intermolecular mechanism in which di- and poly-deuteriopentaboranes are formed. With alkylpentaboranes the absence of di- and poly-alkylpentaboranes in thermal rearrangement makes more probable the hypothesis that the migration of alkyl groups proceeds by an intramolecular path. The reaction mechanism in which there is a slow "symmetrical" splitting of 1-alkylpentaborane and a rapid recombination with formation of a 2-alkylpentaborane, first proposed by Onak[149] on the basis of a theory of Parry[23], seems improbable in the light of later investigations.

A study of the thermal stability of gaseous ethylpentaborane[164] shows that it is less stable than B_5H_9. The decomposition products are H_2, CH_4, involatile boron hydrides, and traces of $B_{10}H_{14}$.

A compound derived from two B_5H_9 molecules containing a methylene bridge, bis-(1-pentaboranyl)methane $(B_5H_8)_2CH_2$, is obtained[165,166] by the reaction of B_5H_9 with alkyl halides (CH_2Cl_2, CH_2Br_2, CH_2BrCl) in the presence of $AlCl_3$. The greatest yield (~ 5%) is obtained when CH_2Cl_2 is used. Its infrared spectrum showed apical boron substitution. $(B_5H_8)_2CH_2$ is a very unstable compound, which reacts rapidly and explosively with air; in a vacuum it slowly decomposes at room temperature. Furthermore, the authors succeeded in obtaining (in insufficiently pure state) the extremely unstable dichloroborylpentabor(9)an--1-ylmethane $B_5H_8CH_2BCl_2$, in which apical substitution also takes place (as indicated by the infrared spectrum). A patent has been obtained[167] for the preparation of bispentaboranylalkanes with two B_5H_8 residues connected by an alkylene bridge by the reaction of a conjugated alkadiene with an excess of B_5H_9 at 135–145°C and elevated pressure.

VI. PENTABORANE(11)

1. Structure of Pentaborane(11)

Pentaborane(11) has been studied less than pentaborane(9). The structure of the B_5H_{11} molecule was determined by X-ray analysis and with the aid of NMR spectra. An X-ray analysis of B_5H_{11} was made by Lavine and Lipscomb[168,169], and then the calculation of the interatomic distances was refined by Lipscomb and coworkers[33]. B_5H_{11} forms monoclinic crystals with group symmetry $P2_1/n$, lattice parameters a = 6.76, b = 8.51, c = 10.14 Å; β = 94°3′; the unit cell contains four B_5H_{11} molecules. The B_5H_{11} molecule has a planar symmetry, the boron atoms forming a skeleton which is a fragment of an icosahedron; it can also be obtained from the B_5H_9 tetragonal pyramid by opening one B–H–B bond of the base (Fig. 10). The interatomic distances in the B_5H_{11} molecule have been determined: $B_{(1)}$–$B_{(3)}$ = 1.71 ± 0.02 Å; $B_{(1)}$–$B_{(2)}$ = 1.87 Å; $B_{(2)}$–$B_{(3)}$ = 1.76 ± 0.01 Å; $B_{(3)}$–$B_{(4)}$ = 1.77 Å; B–$H_{terminal}$ = = 1.10 ± 0.09 Å; $B_{(2)}$–H_{bridge} = 1.17 Å; $B_{(3)}$–H_{bridge} = 1.08 Å; $B_{(3)}$–H_{bridge} = 1.01 Å; $B_{(4)}$–H_{bridge} = 1.24 Å; $B_{(4)}$–H_{bridge} = = 1.37 Å; $B_{(5)}$–H_{bridge} = 1.44 Å; $B_{(1)}$–$H_{(11)}$ = 1.09 Å; $B_{(2)}$–$H_{(11)}$ = 1.77 Å; $B_{(5)}$–$H_{(11)}$ = 1.68 Å. Some contraction (by 0.1 Å) of the B–H bonds is probably explained by a systematic error in the method of calculation. The molecular angles in B_5H_{11} have also been measured[169]. The ^{1}H- and ^{11}B-NMR spectra of pentaborane(11)[92,170] confirm this structure for B_5H_{11}. The ^{1}H-NMR spectrum of B_5H_{11}[170] shows the presence of four types of hydrogen bonds: (1) the

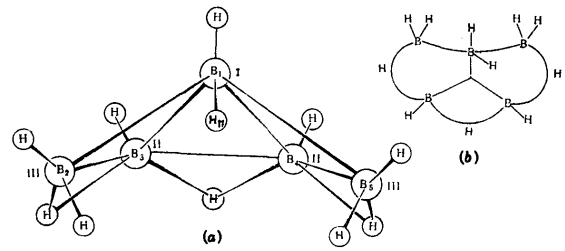


Fig. 10.

six terminal hydrogen atoms form quartets; (2) the apical terminal H_4; (3) three bridge hydrogens (multiplet); (4) the "unique" $H_{(11)}$ forms a sharp peak. The ^{11}B-NMR spectrum of B_5H_{11} shows three types of boron atom. The spectra given by Schaeffer and coworkers[92] differ somewhat from those given by Williams and coworkers[170], but they all contain peaks corresponding to three types of boron atom. The interpretation of the NMR spectra agrees with the structure of B_5H_{11}, but the distribution of charges calculated by Lipscomb[89] disagrees with some conclusions from the spectra. The ^{1}H-NMR spectrum of B_5H_{11}, specially purified by chromatography, recorded by Lutz and Ritter[74], differed slightly from the B_5H_{11} spectra mentioned above and the distribution of the charges of the boron atoms calculated from this spectrum agrees with Lipscomb's calculated data[38].

Eberhardt and coworkers showed[11] that in the B_5H_{11} molecule the apical atom $B_{(1)}$ is connected with two terminal hydrogen atoms, one of which (the "unique" $H_{(11)}$) has in addition a very weak bond with two basal boron atoms. These boron atoms (type B_{III}) are each bound by two-centre bonds with two terminal hydrogen atoms and one bridge hydrogen atom; the remaining basal boron atoms (type B_{II}) have one terminal hydrogen atom and each is bound to two bridge hydrogens. After forming these bonds, at the apical boron atom B_I there remain two orbitals and one electron; one orbital and one electron at the B_{II} atoms; one orbital and a half electron at the B_{III} atoms, that is, six orbitals and four electrons in all, which are used to form the bonds of the apical B_I atom with the basal B_{II} atoms. It is assumed that for the bonds of B_I with B_{II} atoms the sp^2-orbital of B_I and the two sp^3-orbitals of B_{II} are used, which form a central three-centre bond concentrated in the B_{II}–B_I–B_{II} triangle. For the bond of B_I with the B_{III} atoms, the p-orbital of the B_I atom and the sp^3-orbitals of the B_{III} atoms are used and by this means an open three-centre bond is formed. The formal distribution of the charges between the boron atoms was calculated[35]: $B_I = -\frac{2}{3}$, $B_{II} = +\frac{1}{3}$, $B_{III} = 0$. This charge distribution demands asymmetry of the B_{II}–H–B_{III} bridges; however, definite conclusions could not be drawn from their experimental results, measurements of greater accuracy being needed for this.

2. Preparation of Pentaborane(11)

There are several papers on the preparation of B_5H_{11} under laboratory conditions. In 1933 Burg and Schlesinger proposed a method of preparing B_5H_{11} by pyrolysis of diborane at 100–115°C,[47] a method which they subsequently improved[25].

The most convenient method of obtaining B_5H_{11} by pyrolysis of B_2H_6 was proposed by Klein and coworkers [50], using the technique of cold–hot tubes. Conditions were selected under which B_5H_{11} is obtained in 70% yield from B_2H_6: the temperature of the cold tube is -30°C, that of the hot tube +120°C, duration of the experiment 2.5 h, the B_5H_{11} and H_2 formed being removed from the reaction zone every 15 min:

$$2B_2H_6 \rightarrow B_4H_{10} + H_2;$$
$$5B_4H_{10} \rightleftarrows 4B_5H_{11} + 3H_2.$$

The conversion of B_4H_{10} into B_5H_{11} is a reversible reaction:

$$2B_5H_{11} + 2H_2 \rightleftarrows 2B_4H_{10} + B_2H_6.$$

Study of the kinetics of the pyrolysis of diborane at 80–120°C [95] suggests that B_5H_{11} is an intermediate in the formation of most other boron hydrides from B_2H_6. The scheme of the reaction is:

$$B_2H_6 \rightleftarrows 2BH_3, \quad (1)$$
$$B_2H_6 + BH_3 \rightarrow \text{intermediate products}, \quad (2)$$
$$\text{intermediate products} + B_2H_6 \rightarrow B_5H_{11} + 2H_2, \quad (3)$$
$$B_5H_{11} \rightarrow B_5H_9 + H_2, \quad (4)$$
$$B_5H_{11} \rightarrow B_2H_6 - \text{higher boron hydrides}. \quad (5)$$

The pyrolysis of diborane in a pulsation heater [8] showed that B_5H_{11} is formed through a tetraborane(10) fragment (B_4H_8):

$$B_4H_8 + B_2H_6 \rightarrow B_5H_{11} + BH_3; \; B_5H_{11} \rightleftarrows B_4H_8 + BH_3.$$

Experiment confirmed the hypothesis [95,96] that tetraborane is an intermediate in the formation of B_5H_{11} from B_2H_6.

When B_2H_6 is irradiated by light of wavelength 1849 Å a mixture of H_2, B_4H_{10}, B_5H_{11}, and, at low pressure, also the polymer $(BH)_x$ is formed [53]. On the basis of kinetic data it is assumed that B_5H_{11} and B_4H_{10} are obtained independently of one another. The condition for the formation of B_5H_{11} is the dissociation of B_2H_6 into BH_3 radicals and the reaction of the latter in an excited state. Raising the pressure lowers the rate of formation of B_5H_{11} owing to deactivation of B_2H_6 and recombination of BH_3. The mechanism of formation of B_5H_{11} is:

$$B_2H_6 + h\nu \rightarrow B_2H_6 \rightarrow 2BH_3$$
$$\downarrow M$$
$$B_2H_6 + M, \quad (M = \text{third body})$$
$$BH_3 + B_2H_6 \rightarrow B_3H_7 + H_2,$$
$$B_3H_7 + B_2H_6 \rightarrow B_5H_{11} + H_2.$$

There is a difference between the kinetics and the mechanism of thermal and photochemical conversion of B_2H_6 into B_5H_{11}.

A patent has been obtained [171] on a method for the catalytic conversion of B_2H_6 into B_5H_{11} at 175°C. The catalyst is zirconium boride and the yield of B_5H_{11} is 74.5% at a diborane conversion of 7.9%.

The preparation of completely pure B_5H_{11} was described by Spielman and Burg [78]. To purify B_5H_{11} the authors used an efficient low-temperature fractionation column, with a high reflux ratio. The B_5H_9 impurity slowly distilled into a trap (-196°C). The ^{11}B-NMR spectrum shows the complete absence of B_5H_9 impurity and other boron hydrides. B_5H_{11} has the following characteristics [78]: m.p. -122.0 ± ± 0.1°C (value given earlier -123.3°C [41]); vapour pressure 52.8 mmHg at 0°C, 103.1 mmHg at 13.5°C, 116.1 mmHg at 16.1°C. Previously a b.p. of 63°C was found for B_5H_{11} from the equation for the temperature dependence of vapour pressure:

$$\log P_{mmHg} = 7{,}901 - (1690.3/T).$$

Pentaborane(11) is unstable at room temperature and gradually decomposes on storage. At -78°C and prolonged storage mass spectroscopy shows that B_5H_{11} partly decomposes with formation of B_5H_9 and higher boron hydrides (B_6H_{10}, B_9H_{13}, $B_{10}H_{14}$). [172]

3. Isotopic Exchange and Pyrolysis of Pentaborane(11)

The reactions of B_5H_{11} show the instability of the molecule of this boron hydride. Koski has established [64] that when B_5H_{11} reacts with B_2D_6 or $^{10}B_2H_6$ exchange of hydrogen or boron atoms occurs, and study of the kinetics of the reaction in both instances shows that the reaction is half-order in B_5H_{11} and is first-order with respect to B_2D_6 or $^{10}B_2H_6$. Pentaborane(11) is split during this and all the ^{11}B, ^{10}B, H, and D atoms of both molecules participate in the exchange (mass spectra data) and the reaction proceeds by an intermolecular mechanism. Mass spectrometric study under mild conditions of the exchange reaction of B_5H_{11} with B_2D_6 showed that all the D atoms in B_2D_6 are exchanged at the same rate; all the B atoms also have a single rate of exchange, the exchange rate for the D and H atoms being twice that for the ^{10}B–^{11}B exchange. Similar results were obtained in studying the exchange of boron and deuterium between pentaborane(11) and diborane with infrared spectra.

The author proposes the following mechanism for the reaction:

$$B_5H_{11} \rightleftarrows BH_3 + B_4H_8$$
$$BH_3 + B_2D_6 \rightarrow B_2H_3D_3 + BD_3 \quad \left.\right\} \text{rate-determining stages of the process}$$
$$B_4H_8 + B_2D_6 \rightarrow B_5H_5D_6 + BH_3 \quad \left.\right\}$$
$$BH_3 + BD_3 \rightarrow B_2H_3D_3$$

The D (and ^{10}B) atoms thus introduced into the pentaborane molecule can be rapidly redistributed into the various positions of the molecule as a result of intramolecular exchange. The mass spectrum of B_5H_{11} also shows the instability of its molecule [65]. On heating (100°C), pentaborane(11) decomposes with formation of H_2, B_2H_6, B_4H_{10}, B_5H_9, and mixtures of involatile higher boron hydrides, including decaborane [46]. In the presence of hydrogen the main products of the pyrolysis of B_5H_{11} are B_4H_{10} and B_2H_6 (100°C, 10 min).

The equilibrium constants of this reversible reaction were measured in the range 100–140°C and the entropy and enthalpy of the process were determined [173]. On heating B_5H_{11} in the presence of hydrogen [8], in addition to B_2H_6, B_4H_{10}, and higher boron hydrides, B_5H_9 and B_6H_{10} are also formed in small amounts; when a mixture of B_5H_{11} and B_2H_6 (8 and 92% respectively) is heated the main products of the reaction are B_4H_{10}, B_5H_9, B_6H_{10}, and higher boron hydrides.

4. Reaction of B_5H_{11} with Lewis Bases

Stock and Poland [174] studied the reaction of B_5H_{11} with NH_3 at temperatures between -130° and +20°C and found that pentaborane(11) forms an addition compound with ammonia. The structure of the compounds obtained and the course of the reaction were not found. On heating, the addition product was changed into borazole.

Burg and Boone showed, in a series of papers, the ability of B_5H_{11} to be changed into other boron hydrides under the influence of Lewis bases and controlled conditions. This is an interesting property of B_5H_{11}, which once again shows its instability. Under the action of water at low temperature (the reagents were heated from -78° to 0°C until the ice started to melt) and a short time of contact (1 min) pentaborane(11) is partly hydrolysed, with formation of tetraborane(10) in 96% yield[56,57]:

$$B_5H_{11} + 3H_2O \rightarrow B_4H_{10} + B(OH)_3 + 2H_2.$$

The conversions of B_5H_{11} into B_6H_{10} [175,176] (on passing B_5H_{11} over a large surface of diglyme [bis-(2-methoxyethyl) ether] at temperatures from -78° to -20°C the yield of B_6H_{10} is up to 65%) and into B_9H_{15} [176] (with hexamethylenetetramine at 0°C, yield of B_9H_{15} up to 13%) have been proposed as convenient laboratory methods for these boron hydrides which previously were practically inaccessible. These are the main new methods for the conversion of some boron hydrides into others with chemical reagents, and not by thermal decomposition of the molecule.

Detachment of a BH_3 group from the B_5H_{11} molecule and subsequent disproportionation of the fragments occurs under the influence of Lewis bases — $(CH_3)_3N$, $[(CH_3)_2N]_2BH$, $(CH_2)_6(NH_2)_4$, $(CH_3)_2O$, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$ — and in this both boron hydrides with less boron (B_2H_6, B_4H_{10} [56,175]) and also higher boron hydrides [175,176] are formed (B_6H_{10}, B_9H_{15}, $B_{10}H_{14}$); part of the pentaborane(11) is always converted into stable pentaborane(9). $(CH_3)_2O$ and B_5H_{11} at -78°C form an addition product with the empirical formula $B_5H_{11}.1.5(CH_3)_2O$.[176] It is assumed that the ether is coordinated to two type B_{II} boron atoms. The bonding of the ether to these boron atoms weakens the bond with the bridge hydrogens and facilitates the conversion of the B_5H_{11} molecule into other boron hydrides. A similar explanation is given for the conversion of B_5H_{11} into B_4H_{10} under the influence of water: the detachment of a B–H fragment, obtained from a B_{II} atom coordinated with oxygen and the formation of a B_4H_{10} molecule with minimal and localised rearrangement of the structure. The reaction of pentaborane(11) with amines also probably starts with electron-donor attack of the atom at these B_{II} atoms (specially bound) and with the formation of corresponding addition compounds.

In the reaction of $(CH_3)_3N$ with B_5H_{11},[175] as well as boron hydrides, trimethylamine-borane $(CH_3)_3N.BH_3$ is formed, the yield of which rises as the ratio $(CH_3)_3N : B_5H_{11}$ is raised to 2:1. Much less boron hydrides are then formed. It was also found[176] that $(CH_3)_3N.BH_3$ is a catalyst for the conversion of B_5H_{11} into other boron hydrides, which shows the greater acceptor ability of B_5H_{11} in comparison with BH_3. It has been shown that the strength of the Lewis base affects the composition of reaction products in the disproportionation of B_5H_{11}: addition products of B_5H_{11} with weak Lewis bases are readily decomposed with liberation of BH_3. Then high yields of B_2H_6 and B_4H_{10} are obtained; too strong Lewis bases form stable complexes with BH_3 group scission from the B_5H_{11}, continually removing it from the reaction zone, leading to a decrease in the yield of higher boron hydrides, particularly B_6H_{10}. The best yield of B_6H_{10} is obtained when Lewis bases of medium strength are employed, for example, diglyme.

When carbon monoxide acts on B_5H_{11} under mild conditions (20–25°C, CO pressure 7–20 atm) scission of the molecule (typical for B_5H_{11}) into BH_3 and B_4H_8 and formation of B_4H_8CO occur[77]. A detailed description of the preparation of B_4H_8CO and of its physical and chemical properties has appeared[78].

The course of the reaction of B_5H_{11} with CO is expressed by the equations:

$$B_5H_{11} \rightarrow B_4H_8 + BH_3,$$
$$B_4H_8 + CO \rightarrow B_4H_8CO,$$
$$BH_3 + CO \rightarrow BH_3CO.$$

The method of obtaining B_4H_8CO from B_5H_{11} is simpler and faster than that from B_4H_{10}, but completely pure pentaborane(11) is necessary for it, and this is not readily available. Therefore at present the preparation of B_4H_8CO from B_4H_{10} is more rational.

PF_3 reacts with B_5H_{11} like CO [78] with the formation of $B_4H_8.PF_3$ and $BH_3.PF_3$ under mild conditions (at ~ 30°C for 2 h). $B_4H_8.PF_3$ is quantitatively and reversibly converted into B_4H_8CO with CO (1 h at 18°C):

$$B_4H_8 \cdot PF_3 + CO \rightleftarrows B_4H_8 \cdot CO + PF_3.$$

5. Alkyl Derivatives of Pentaborane(11)

Various alkylating agents have been used to alkylate B_5H_{11}, these reactions also showing the lability of the pentaborane(11) molecule and its tendency to split into B_4H_8 and BH_3 groups. The alkyl derivatives of B_5H_{11} are unstable compounds.

Lutz and Ritter[74] obtained methyl derivatives of pentaborane(11) by its reactions with $CH_3B_2H_5$ under mild conditions (at 35°C for 30 min) or by reaction of B_4H_{10} with 1,2-dimethyldiborane at 100° for 15 min:

$$B_5H_{11} + B_2H_5CH_3 \rightleftarrows B_5H_{10}CH_3 + B_2H_6,$$
$$B_4H_{10} + {}^1/_2(BH_2CH_3)_2 \rightleftarrows B_5H_{10}CH_3 + H_2.$$

Methylpentaborane(11) $B_5H_{10}CH_3$ rather rapidly disproportionates at room temperature (16% after 30 min) with formation of B_5H_{11} and $B_5H_9(CH_3)_2$; on heating (90°C), the substance partly decomposes with liberation of B_5H_{11}, B_2H_6, $B_2H_5CH_3$, $B_5H_8CH_3$, traces of B_5H_9, solid boron hydrides, and $B_5H_9(CH_3)_2$. During the reaction of methylpentaborane(11) with diborane there is an exchange reaction with formation of $B_2H_5CH_3$ and B_5H_{11}: 72% of the $B_5H_{10}CH_3$ reacts after 30 min at 25°C. At a low temperature (from -78° to 0°C) diethyl ether decomposes $B_5H_{10}CH_3$ with release of B_5H_9, B_5H_{11}, and a little $B_5H_9(CH_3)_2$. $B_5H_{10}CH_3$ and $B_5H_9(CH_3)_2$ were identified and characterised with the help of infrared, NMR, and mass spectra. In the mass spectrum of $B_5H_{10}CH_3$ the most intense peaks correspond to the ions $B_5H_6CH_3^+$, $B_5H_8CH_3^+$, and $B_5H_4CH_3^+$; in the mass spectrum of $B_5H_9(CH_3)_2$ the most intense peaks are those of the ions $B_5H_5(CH_3)_2^+$, $B_5H_7(CH_3)_2^+$, and $B_5H_3(CH_3)_2^+$; that is, in methylpentaborane(11) and in dimethylpentaborane(11) the B–H bonds are split more easily than the B–C bond; furthermore, the tendency to the loss of hydrogen atoms in pairs is kept.

$B_5H_9(CH_3)_2$ is partly disproportionated at room temperature; the mass spectrum of a specimen of $B_5H_9(CH_3)_2$ which has been kept standing at 20–25°C contains peaks corresponding to $B_5H_8(CH_3)_3$.

The ^1H-NMR spectra of $B_5H_{10}CH_3$ and B_5H_{11} show that: (1) the CH_3 group is localised at B_{III} atoms; (2) geometrical isomerism exists in the $B_5H_{10}CH_3$ molecule; (3) an inductive effect may appear in a delocalised polyhedral

system. The infrared spectra of $B_5H_{10}CH_3$ and $B_5H_9(CH_3)_2$ confirm these conclusions.

Maguire and coworkers [177] studied the reaction of ethylene with pentaborane(11). After 30 min at 25°C and a pressure of 500 mmHg $C_2H_5B_5H_{10}$ is formed in 96% yield at 18% conversion of the B_5H_{11}; furthermore, small quantities of B_4H_{10}, H_2, $C_2H_5B_2H_5$, $C_2H_4B_4H_8$, and traces of $(C_2H_5)_2B_5H_9$ are formed. The formation of dimethylenetetraborane identical with the reaction product of B_4H_{10} and C_2H_4 was unexpected. The authors showed that $B_4H_8C_2H_4$ is not a decomposition product of $B_5H_{10}C_2H_5$ but is formed independently, together with $C_2H_5B_5H_{10}$:

$$B_5H_{11} \rightleftarrows B_4H_8 + BH_3,$$
$$C_2H_4 + B_4H_8 \rightarrow C_2H_4B_4H_8,$$
$$C_2H_4 + BH_3 \rightarrow C_2H_5BH_2,$$
$$C_2H_5BH_2 + B_4H_8 \rightarrow C_2H_5B_5H_{10}.$$

The decomposition of $C_2H_5B_5H_{10}$ in the liquid and gas phase in the presence of other boron hydrides has been studied to try to establish the mechanism of the reaction. A very complex mixture of products is obtained here, and the authors could not draw any definite conclusions.

The same authors studied the exchange reaction of $C_2H_5B_2H_5$ with B_5H_{11} [178] under mild conditions (30 min, 0°C) and found that there are then competing reactions of exchange of H at the C_2H_5 group and symmetrisation of $C_2H_5B_2H_5$:

$$C_2H_5B_2H_5 \xrightarrow{} {}^1/_2\,B_2H_6 + {}^1/_2(C_2H_5)_2B_2H_4$$
$$C_2H_5B_2H_5 \xrightarrow{B_5H_{11}} B_2H_6 + C_2H_5B_5H_{10}$$

Pentaborane(11) also undergoes an exchange reaction with symmetrical $(C_2H_5)_2B_2H_4$ to give $(C_2H_5)_2B_5H_9$ with C_2H_5 groups at different boron atoms. Other boron hydrides (B_4H_{10}, B_5H_9, $B_{10}H_{14}$) which have been studied under these conditions do not react with $C_2H_5B_2H_5$ and $(C_2H_5)_2B_2H_4$. These reactions are yet another proof of the lability of the H and B atoms in the B_5H_{11} molecule, and probably proceed with scission of the reacting molecules:

$$B_5H_{11} \rightleftarrows BH_3 + B_4H_8; \quad RB_2H_5 \rightleftarrows RBH_2 + BH_3.$$

The exchange reaction between $C_2H_5B_2H_5$ and B_5H_{11} reaches an equilibrium.

There are several patents on methods of alkylating B_5H_{11}. The reaction of an alkyl halide (C_2H_5Br, n-C_3H_7Cl, n-C_4H_9Cl) with a mixture of pentaboranes (70–90% B_5H_{11} and 10–30% B_5H_9) in the presence of $AlCl_3$ under mild conditions (20°C, 560 mmHg) for 1 h gives a mixture of alkylated pentaboranes [179] which was separated by fractionation. Liquid products were obtained in the reaction of B_5H_{11} with conjugated dienes [180] at 20–40°C but their composition is not given.

VII. HEXABORANE(10)

1. Structure of Hexaborane(10)

The molecular structure of hexaborane(10), B_6H_{10}, was established by X-ray analysis and NMR-spectroscopy. Lipscomb and coworkers [181,182] showed that the boron atoms in B_6H_{10} form a pentagonal pyramid (Fig. 11), which is a fragment of an icosahedron, and they determined the interatomic distances by an X-ray diffraction method.

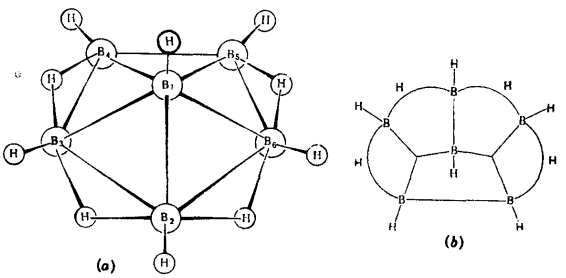


Fig. 11.

They give [182] the following data: $B_{(1)}-B_{(4)} = B_{(1)}-B_{(5)} = 1.795 \pm 0.01$ Å; $B_{(1)}-B_{(3)} = B_{(1)}-B_{(6)} = 1.753 \pm 0.009$ Å; $B_{(1)}-B_{(2)} = 1.740 \pm 0.014$ Å; $B_{(4)}-B_{(5)} = 1.596 \pm 0.012$ Å; $B_{(4)}-B_{(3)} = B_{(5)}-B_{(6)} = 1.737 \pm 0.001$ Å; $B_{(3)}-B_{(2)} = B_{(6)}-B_{(2)} = 1.79 \pm 0.009$ Å; $B-H_{terminal} = 1.21 \pm 0.07$ Å; $B_{(4)}-H_{bridge} = 1.35$ Å; $B_{(8)}-H_{bridge} = 1.31$ Å; $B_{(3)}-H_{bridge} = 1.48$ Å; $B_{(4)}-H_{bridge} = 1.32$ Å.

For the six boron atoms which form a pentagonal pyramid, two types of distributions of the bonds have been proposed [183]. After detailed study and calculations for the B_6H_{10} molecule Lipscomb and coworkers [10,182] proposed a structure which does not contain BH_2 groups, has four B–H–B bridge bonds, and a planar symmetry. Each of the five boron atoms which form the base of the pyramid are connected to a terminal hydrogen atom; in the base there are four B–H–B three-centre bonds and one B–B two-centre bond, connecting the atoms $B_{(4)}$ and $B_{(5)}$. The last atoms use one orbital and half an electron for a bond with the apical boron atom; the atoms $B_{(3)}$, $B_{(2)}$, and $B_{(6)}$ use for this purpose one sp^3-orbital and one electron. The apical boron atom is connected with one terminal hydrogen, the remaining three orbitals and two electrons being used for bonds with the basal boron atoms: one two-centre bond $B_{(1)}-B_{(2)}$ and two central three-centre bonds between the atoms $B_{(4)}-B_{(1)}-B_{(3)}$ and $B_{(5)}-B_{(1)}-B_{(6)}$ are formed on both sides of the plane of symmetry. The authors explain the unusually short distance between atoms $B_{(4)}$ and $B_{(5)}$ (1.596 Å) by all the bonds formed by these atoms (the $B_{(4)}-B_{(1)}-B_{(3)}$ and $B_{(4)}-H-B_{(3)}$ three-centre bonds and the B–H and $B_{(4)}-B_{(5)}$ two-centre bonds) exhibiting quite marked departures of the valence angle from the tetrahedral configuration and a corresponding bond shortening. This situation is comparable with that in the cyclopropane ring, where the strong strain in the ring leads to unusually short interatomic distances. Starting from the assumed structure for B_6H_{10}, the charges of the boron atoms were calculated [182]: $-\frac{1}{3}$, $-\frac{1}{6}$, $+\frac{1}{3}$, and 0 for the atoms $B_{(1)}$, $B_{(4)}$, $B_{(3)}$, and $B_{(2)}$†. The NMR spectral data [184] agree with this structure of hexaborane in the main. The ^{11}B-NMR spectrum contains two doublets with relatively intense peaks 5 : 5 : 1 : 1, corresponding to the B–H groups of the base and the B–H group at the apex of the pyramid. The basal boron atoms in the B_6H_{10} molecule are more electropositive [184] than the corresponding boron atoms in B_5H_9. However, the conclusion can be drawn from the ^{11}B-NMR spectrum of B_6H_{10} that all the boron atoms lying in the base of the pentagonal pyramid are identical; that is, the third type of boron atom, indicated by

† The original reference lists these charges in the order $B_{(1)}$, $B_{(2)}$, $B_{(3)}$, $B_{(4)}$ (Ed. of Translation).

Lipscomb's results, is not observed. The identity of these boron atoms is explained [185] by a tautomeric conversion of the two isomers of B_6H_{10}, which differ from one another in the type of bonds. The second isomer of B_6H_{10}, which is less stable, also has a structure of a pentagonal pyramid, but in it the basal boron atoms form three B–H–B three-centre bonds and the $B_{(4)}$ atom is bound to two terminal hydrogens, that is, there is a BH_2 group in the base.

The energies of the bonds in B_6H_{10} have been calculated from the lengths of the B–B and B–H bonds. The calculations show that some of the data on interatomic distances need to be determined more accurately.

2. Preparation and Properties of Hexaborane(10)

Hexaborane(10) was first obtained by Stock [41,94] in very small quantities by the hydrolysis of metal borides with acids; it was mixed with other boron hydrides and was practically inaccessible. Later Lipscomb and coworkers [181], and then Kotlensky and Schaeffer [186] obtained B_6H_{10} by the action of a silent electric discharge (15 kV) on diborane, followed by low-temperature fractionation of the mixture. The yield of B_6H_{10} was small (~ 1%), the main reaction products being B_4H_{10}, B_5H_9, and B_5H_{11} (yields of 40, 20, and 30% respectively); in addition, small amounts of B_9H_{15} and $B_{10}H_{14}$ are formed.

Hexaborane(10) became available after Boone and Burg [57,175,176,187] developed a method of making it from B_5H_{11} by the action of basic reagents. On passing B_5H_{11} vapour over a large surface of diglyme at a low pressure pure B_6H_{10} was obtained in 65% yield [176]. This method of obtaining hexaborane(10) is most convenient. A proposal has been made [188] to obtain B_6H_{10} by the hydrolysis of Mg_3B_2 under somewhat modified conditions compared with those of Stock. The total yield of boron hydrides does not exceed 12%, B_6H_{10} being obtained in a yield from 2 to 6%.

The physical properties of B_6H_{10} have been determined: m.p. -62.3°C [176] or -63.2° ± 0.1°C; [189] b.p. 108°C [176] or 82.2°C (calculated) [189]; the temperature dependence of vapour pressure is described by the equation $\log P_{mmHg} = 5.2124 - (1566.3/T) + 0.005841T$. [189] The heat of vaporisation of B_6H_{10} and its Trouton constant (= 25.7) have also been found [189], the latter showing that the B_6H_{10} molecule is not associated in the liquid state. The mass spectrum of pure B_6H_{10} [189] (differing somewhat from the mass spectrum recorded earlier for insufficiently pure B_6H_{10} [186]) shows that the most stable ion is $B_6H_8^+$; the general tendency for all boron hydrides to lose hydrogen atoms in pairs is observed. The infrared spectrum of B_6H_{10} contains bands corresponding to $B{-}H_{terminal}$ and $B{-}H_{bridge}$ bonds; bands of the BH_2 groups are absent [189]. B_6H_{10} slowly decomposes above 0°C, [189] although it is more stable than B_5H_{11} (a method has been proposed for purifying B_6H_{10} from B_5H_{11}, based on the lower stability of B_5H_{11} at -80°C and at +100°C in the presence of hydrogen). B_6H_{10} is thermally a little more stable than B_4H_{10}. [94]

A preliminary study of the deuterium exchange of B_6H_{10} with B_2D_6 showed [189] that the terminal hydrogen atoms of B_6H_{10} react more rapidly than the bridge hydrogens.

The chemical reactions of B_6H_{10} have been little studied. B_6H_{10} reacts slowly with water in the cold [94], and on heating the reaction:

$$B_6H_{10} + 18H_2O \rightarrow 6H_3BO_3 + 14H_2,$$

occurs. The hydrolysis is faster in acid than in alkali.

VIII. HEXABORANE(12)

1. Structure of Hexaborane(12)

The structure of hexaborane(12) has not been determined experimentally, but Lipscomb has proposed [185] for it the structure of a pentagonal pyramid by analogy with the structure of B_6H_{10} and on the basis of the principles of boron hydride topology. The proposed structure contains two BH_2 groups, four B–H–B bridge bonds, two B–B–B central three-centre bonds, and one B–B two-centre bond; the B_6H_{12} molecule has eight terminal hydrogen atoms and four bridging hydrogen atoms. The other possible structure for B_6H_{12} is apparently less stable, has three BH_2 groups, three B–H–B bridge bonds, and an apical boron atom, connected by three B–B–B three-centre bonds with boron atoms lying in the base of the pyramid. Gaines and Schaeffer [190] on the basis of the topology of the molecule (4212), the ^{11}B-NMR spectra, and the method of preparation from B_3H_7, proposed for B_6H_{12} a structure of an open type unusual for boron hydrides, and which is not a fragment of an icosahedron. Lutz and coworkers [191] consider that the structure of B_6H_{12} is similar to the structure of B_5H_{11} and gives a structure obtained from the B_5H_{11} molecule by replacing one B–H–B bond by a BH_2 group. This structure also agrees with the topology of the molecule, and in the main, with the ^{11}B-NMR spectrum. The absence of X-ray diffraction data does not at present permit a choice to be made between these structures.

2. Preparation and Properties of Hexaborane(12)

Gibbins and Shapiro [192] first isolated B_6H_{12} from the mixture of boron hydrides obtained by the action of an electric discharge on B_2H_6 [186] and identified it by mass spectroscopy. The authors showed that B_6H_{12} is much less stable than B_6H_{10}; it decomposes at room temperature. Gaines and Schaeffer [190,193] obtained B_6H_{12} in ~ 4% yield by the reaction of $(CH_3)_4NB_3H_8$ with polyphosphoric acid and isolated it by high-vacuum distillation. B_6H_{12} slowly decomposes at ~ 20°C with liberation of hydrogen and boron hydrides; the decomposition is accelerated in the presence of water or $(CH_3)_2O$. NMR spectra of B_6H_{12} and its vapour pressure (17 mmHg at 0°C) have been given. Lutz and coworkers [191] isolated and identified B_6H_{12}, which they obtained in low yields (~ 1%) in the decomposition of B_4H_{10} and B_5H_{11} under different conditions. Hexaborane(12) has been purified by gas–liquid chromatography. Its physical properties are: m.p. -82.3°C, vapour pressure 17.1 mmHg at 0°C, 3.8 mmHg at 23.6°C. [191] Study of the decomposition of hexaborane(12) at 25°C (pure and in the presence of B_2H_6) showed that the chemical stability of B_6H_{12} increases with increase in the purity of the compound [191]; the infrared and mass spectra of B_6H_{12} have been recorded. The chemical properties of B_6H_{12} have hardly been studied at all. With water or $(CH_3)_2O$, hexaborane(12) decomposes rapidly according to the equations [191]:

$$B_6H_{12} + 6H_2O \rightarrow B_4H_{10} + 2B(OH)_3 + 4H_2,$$

$$2B_6H_{12} \xrightarrow{(CH_3)_2O} 2B_5H_9 + B_2H_6.$$

IX. HEPTABORANES

Heptaboranes have not been obtained pure, although in several papers [8,186,192,194] it has been shown that they are present in mixtures of boron hydrides. Lipscomb [185] considers possible the existence of three B_7 boron hydrides:

B_7H_{11}, B_7H_{13}, and B_7H_{15}, and proposes for each of them a structure with a less compact arrangement of the boron atoms than for the other boron hydrides, which explains the extremely low stability of these compounds. Schaeffer and coworkers [195] in a mass spectrometric examination of tetraborane obtained from B_2H_6 observed in individual specimens peaks of a previously unknown boron hydride, to which the authors ascribed the formula B_7H_{13}. In the same work there is a statement on the existence of B_7H_{15}. Fehlner and Koski [8] showed that, in the distillation and mass spectrometric analysis of the products of the pyrolysis of B_2H_6, two heptaboranes B_7H_{11} and B_7H_{13} are probably formed (although they did not exclude the possibility of the formation of another pair of heptaboranes: B_7H_{13} and B_7H_{15}). Heptaboranes have not been isolated from mixtures of boron hydrides.

Ditter and coworkers [196] have doubted the existence of heptaboranes on the basis of the mass spectra of specimens of the "heptaborane" fraction after its purification on a chromatograph. The authors consider that ethylpentaboranes, triethoxyboranes, and other impurities, formed from traces of ethane and diethyl ether usually present in boron hydrides, have been erroneously taken for heptaboranes.

X. OCTABORANE(12) B_8H_{12}

The first indication of the formation of octaborane(12) in the pyrolysis of B_5H_{11}, based on measurements of the vapour pressure of the compound obtained, was in a study by Burg and Schlesinger [47], but it was found later [176] that B_9H_{15} is formed in this. Shapiro and coworkers [197,198] recorded the mass spectrum of octaborane(12) present in a mixture with other boron hydrides, and on the basis of this the compound was given the formula B_8H_{12}. Lipscomb and coworkers [199] succeeded in obtaining, isolating in the pure form, and finding the structure of octaborane(12). B_8H_{12} was obtained by the action of an electric discharge on a mixture of B_2H_6 and B_5H_9 (molar ratio 2 : 1), and rapid separation of the reaction products by vacuum low-temperature fractionation with simultaneous mass spectrometric analysis of the fraction. X-Ray analysis of the compound showed that the B_8H_{12} molecule has a plane of symmetry and is a fragment of an icosahedron. Fig. 12 shows the structure of B_8H_{12}.

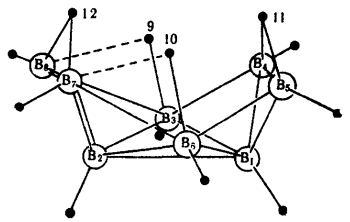


Fig. 12.

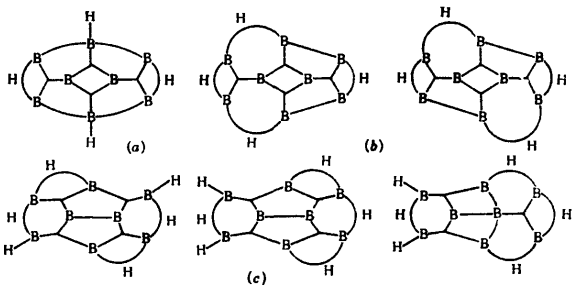


Fig. 13.

The following interatomic distances have been determined: $B_{(1)}-B_{(3)} = B_{(2)}-B_{(3)} = B_{(3)}-B_{(4)} = B_{(5)}-B_{(6)} = B_{(6)}-B_{(7)} = B_{(2)}-B_{(6)} = 1.790 \pm 0.007$ Å; $B_{(1)}-B_{(4)} = B_{(1)}-B_{(5)} = 1.690 \pm 0.006$ Å; $B_{(2)}-B_{(7)} = B_{(2)}-B_{(8)} = 1.720 \pm 0.002$ Å; $B_{(1)}-B_{(2)} = 1.803$ Å; $B_{(3)}-B_{(8)} = 1.800$ Å; $B_{(4)}-B_{(5)} = 1.672$ Å; $B_{(7)}-B_{(8)} = 1.706$ Å; $B-H_{terminal} = 1.10 \pm 0.03$ Å; $B_{(3)}-H_{(9)} = B_{(6)}-H_{(10)} = 1.28 \pm 0.02$ Å; $B_{(8)}-H_{(9)} = B_{(7)}-H_{(10)} = 1.47 \pm 0.01$ Å. Each boron atom in the B_8H_{12} molecule has one terminal hydrogen atom; furthermore, there are two symmetrical hydrogen bridges $B_{(4)}-H_{(11)}-B_{(5)}$ and $B_{(7)}-H_{(12)}-B_{(8)}$ and two unsymmetrical bridges $B_{(3)}-H_{(9)}-B_{(8)}$ and $B_{(6)}-H_{(10)}-B_{(7)}$, in which the hydrogen atom is situated close to the $B_{(3)}$ and $B_{(6)}$ atoms. The character of the bonds between the boron atoms was not analysed in this work; however, previously Lipscomb [1], on the basis of the topology of B_8H_{12} (4420) had proposed a structure (Fig. 13) in which the molecule contains four central B–B–B three-centre bonds and two B–B two-centre bonds, in addition to bonds with hydrogen atoms. B_8H_{12} is an extremely unstable compound; therefore the study of its structure is done at a low temperature (below -20°C).

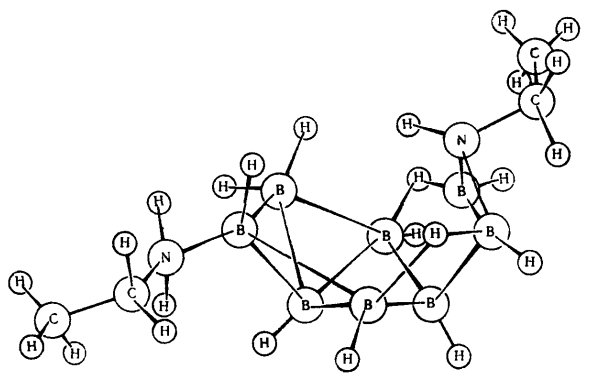


Fig. 14.

In addition to B_8H_{12}, a derivative of octaborane of the composition $C_2H_5NH_2B_8H_{11}NHC_2H_5$ has been obtained [200] by the action of $C_2H_5NH_2$ on a nonaborane complex, $B_9H_{13}S.(C_2H_5)_2$; it was isolated in the pure state and studied by X-ray diffraction [200,201]. It was shown that there is a B–N–B bridge bond in this compound, like the bond in aminodiborane, formally replacing one B–H–B bond. This type of bond was first observed in the higher boron hydrides in this example. It is assumed that this compound is a derivative of the hypothetical ion $B_8H_{13}^-$; its structure is shown in Fig. 14.

The geometry of the molecule shows that the lattice of boron atoms is a fragment of an icosahedron. All the interatomic distances were determined and the precise positions

of all the boron, nitrogen, and carbon atoms were found, and of all the hydrogen except one hydrogen atom in the NH_2 group and three hydrogens in one CH_3 group. The compound is rather stable thermally and chemically, probably owing to stabilisation by the ethylamine molecules. If the bridge nitrogen atom is formally replaced by hydrogen, then (by analogy with $B_2H_5NR_2$ and B_2H_6) B_8H_{12}.L (where L denotes ligand) is obtained, from which it is possible to obtain the hypothetical $B_8H_{13}^-$ ion, which is a derivative of B_8H_{14}. The authors suggested the instability of this octaborane is due to steric hindrance.

Hence the octaboranes are also extremely unstable representatives of the boron hydrides and at present have been very little studied.

XI. NONABORANE(15)

Nonaborane(15), B_9H_{15}, is yet another boron hydride which has been obtained comparatively recently. Mention of some nonaborane among the decomposition products of pentaborane(11) when the latter is kept for a long period is made by Norton [172]. B_9H_{15} was first obtained by Kotlensky and Schaeffer [186] as a by-product produced in extremely small amounts in a mixture with B_6H_{10} and $B_{10}H_{14}$ (total amount of the three boron hydrides ~ 1%) by the action of a silent electric discharge on diborane. Its formula and structure were established by X-ray analysis and mass spectrometrically [202,203], in which extremely small quantities of material were used and were of insufficient purity. In 1962, Burg and Kratzer [176] developed a method for obtaining B_9H_{15} by the catalytic decomposition of B_5H_{11} in the presence of hexamethylenetetramine at 0°C, yield of B_9H_{15} ~ 13%. The constants obtained for pure nonaborane (m.p. +2.8°C, vapour pressure 0.8 mmHg at 28°C) differ considerably from those of the specimen used earlier by Lipscomb [202,204] for establishing the structure of B_9H_{15} (m.p. -18° to -20°C); however, Burg and Kratzer showed with the aid of ^{11}B-NMR, infrared, and mass spectra that the specimens were identical in chemical structure, and the difference in constants is explained by the presence of other boron hydrides as impurities. Ditter and coworkers [196] obtained nonaborane(15) from B_5H_{11} and B_2H_6 (excess of diborane, pressure 27 atm) and recorded the mass spectrum of pure B_9H_{15}.

Nonaborane(15) has the structure shown in Fig. 15.

The interatomic distances [202] are (in Å): $B_{(1)}-B_{(3)} = B_{(1)}-B_{(8)} = 1.76$; $B_{(3)}-B_{(8)} = 1.80$; $B_{(3)}-B_{(9)} = B_{(8)}-B_{(9)} = 1.86$; $B_{(3)}-B_{(4)} = B_{(7)}-B_{(8)} = 1.95$; $B_{(1)}-B_{(4)} = B_{(1)}-B_{(7)} = 1.75$; $B_{(1)}-B_{(2)} = 1.77$; $B_{(2)}-B_{(4)} = B_{(2)}-B_{(7)} = 1.82$; $B_{(2)}-B_{(5)} = B_{(2)}-B_{(6)} = 1.76$; $B_{(5)}-B_{(6)} = 1.78$; $B_{(4)}-B_{(5)} = B_{(6)}-B_{(7)} = 1.84$; $B-H_{terminal} = 1.15 \pm 0.32$; $B-H_{bridge} = 1.36 \pm 0.32$; accuracy of B–B distances 0.07 Å.

The boron atoms in the B_9H_{15} molecule are disposed in the form of a fragment of an icosahedron, but there is some deformation of the boron framework owing to an increase in the distances $B_{(3)}-B_{(4)}$ and $B_{(7)}-B_{(8)}$. Each boron atom is connected to a terminal hydrogen atom, the direction of these bonds approximately coinciding with the lines leading from the centre of the icosahedron to the boron atom concerned. The atom $B_{(9)}$ has two terminal hydrogen atoms so that these atoms are directed perpendicular to the plane formed by the atoms $B_{(8)}B_{(9)}B_{(3)}$, and are situated on opposite sides of this plane. In the B_9H_{15} molecule there are five B–H–B bridge bonds and six types

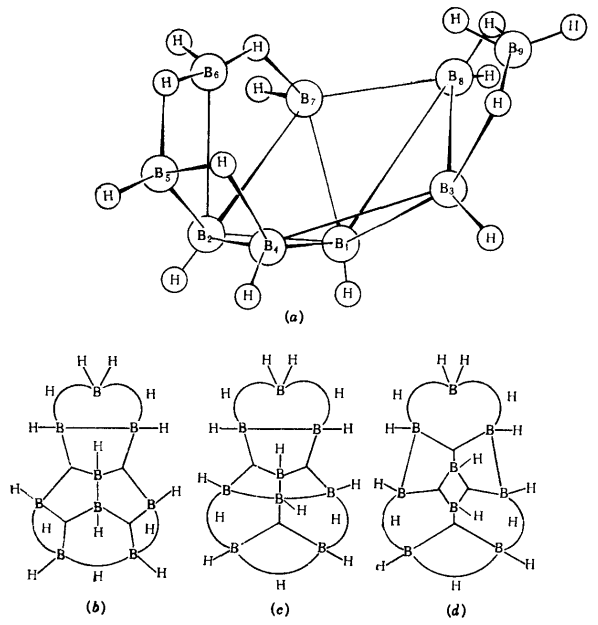


Fig. 15.

of boron atoms. The structure of the valence bonds in the molecule around the atoms $B_{(2)}-B_{(4)}-B_{(5)}-B_{(6)}-B_{(7)}$ is reminiscent of the structure of the B_5H_{11} molecule; just as in this compound, three B–H–B bridge bonds are directed inwards towards the centre of the icosahedron. On the other hand (near the BH_2 group) the bonding of the molecule is reminiscent of B_4H_{10}. In the molecule of B_9H_{15} the boron atoms are bound to one another (apart from the five B–H–B bridge bonds) by another two two-centre and four three-centre bonds. A topological calculation has shown [183] that such a structure is the best for B_9H_{15}. There are three possible ways of arranging the three-centre bonds between the boron atoms in a B_9H_{15} molecule which is a fragment of an icosahedron, when a plane of symmetry is present (Figs. 15*b*–15*d*). All these structures can be converted into one another by a small change in atomic orbitals. The LCAO–MO method was used to calculate the charge distribution between the boron atoms, the bond energies, and the ionisation potentials [38] for the ideal B_9H_{15} molecule. The ^{11}B-NMR spectrum of B_9H_{15} [176] contains two triplets in the low and high potential regions; the interpretation of this spectrum is complex but it evidently agrees with the structure of B_9H_{15} obtained by the X-ray analysis of the compound. The infrared spectrum is also very complex; it contains lines corresponding to three types of B–H–B bond, five types of terminal B–H bond, and also several types of B–B bond.

2. Properties of B_9H_{15}

Some information has been obtained on the stability of B_9H_{15}: [176] the compound is unchanged after 1 h at 0°C; on holding for 40 s at 74.9°C and 3.89 mmHg (to determine the molecular weight), the melting point of the compound is lowered to 0.6–0°C and a little hydrogen is released (0.016 moles hydrogen per mole B_9H_{15}), that is, there is slight decomposition of the B_9H_{15}. However, the stability of B_9H_{15} surpasses that of B_8H_{12} and the B_7 hydrides and is

comparable with that of B_5H_{11}. The kinetics of the decomposition of nonaborane(15) into B_8H_{12} and B_6H_{10} have been studied with the mass spectrograph[196].

Nonaborane derivatives of the type $B_9H_{13}.L$ (where L is a ligand) are derivatives of the hypothetical anion $B_9H_{14}^-$ and were first obtained and characterised by Graybill and coworkers[205,206] by the action of diethylamine on decaborane(14) followed by treatment with aqueous HCl, when the following reactions take place:

$$B_{10}H_{14} + (C_2H_5)_2NH \xrightleftharpoons{\text{rapid}} (C_2H_5)_2\overset{+}{N}H_2B_{10}H_{13}^- \xrightarrow[\text{slow}]{(C_2H_5)_2NH}$$

$$\rightarrow (C_2H_5)\overset{+}{N}H_2B_{10}H_{13}^- \cdot [(C_2H_5)_2NH],$$

$$B_{10}H_{13}^- \cdot [(C_2H_5)_2NH] + H_3\overset{+}{O} + 2H_2O \rightarrow 2H_2 + B(OH)_3 + B_9H_{13} \cdot [(C_2H_5)_2NH].$$

The same compounds are obtained by alcoholysis of $B_{10}H_{12}L_2$ (L = CH_3CN or Et_2S):

$$B_{10}H_{12}L_2 + ROH \rightarrow B_{10}H_{13}L \cdot (ROH) + L,$$

$$B_{10}H_{12}L \cdot (ROH) + 2ROH \rightarrow B_9H_{13}L + B(OR)_3 + H_2.$$

The authors showed that in the compound $B_9H_{13}S(C_2H_5)_2$ the ligand undergoes substitutions with CH_3CN, $P(C_5H_5)_3$, pyridine and its derivatives, $(C_2H_5)_2NH$, or $(C_2H_5)_3N$. When this compound is treated with an excess of diethylamine there is partial degradation of the anion and formation of a derivative of octaborane, $C_2H_5NH_2B_8H_{11}NHC_2H_5$.[200] When $B_9H_{13}S(C_2H_5)_2$ is treated with strong bases L is replaced and a derivative of a new anion, $B_9H_{12}^-$, is formed[205]:

$$B_9H_{13}S(C_2H_5)_2 + (CH_3)_4NOH \rightarrow (CH_3)_4N^+ + B_9H_{12}^- + H_2O + S(C_2H_5)_2.$$

The compounds $B_9H_{13}.L$ can give derivatives of $B_9H_{12}^-$ also on reaction with pyridine. The anion $B_9H_{12}^-$ is much less stable than $B_9H_{14}^-$; its structure has not been established. Methanolysis of $B_9H_{12}N(CH_3)_4$ leads to decomposition of the anion $B_9H_{12}^-$ and the relatively stable anion $B_3H_8^-$, which is a method of obtaining the latter[18].

The structure of $B_9H_{13}CNCH_3$ was found by X-ray diffraction[207,208], and is shown in Fig. 16.

The boron atoms form a fragment of an icosahedron and are arranged like nine of the boron atoms in the $B_{10}H_{12}(CNCH_3)_2$ molecule, from which $B_9H_{13}CNCH_3$ is obtained; two of the boron atoms have two terminal hydrogens, the rest each have one hydrogen atom; in addition, there are two B–H–B bridge bonds in the molecule. The character of the bonds between the boron atoms in the $B_9H_{13}CNCH_3$ molecule is somewhat different from that of the B_9H_{15} molecule; the authors attribute this difference to tautomerism of the hydrogen atoms in the boron hydride

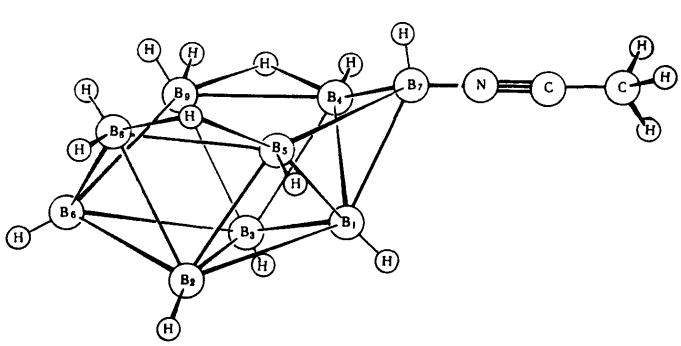


Fig. 16.

as a result of which yet another BH_2 group and a negative ion (or its derivative) are formed. Graybill and coworkers[205] suggest that the boron atom connected to the ligand molecule has sp^2-hybridisation (analogous to the atoms $B_{(6)}$ and $B_{(9)}$ in $B_{10}H_{12}.L_2$). The authors found that in the excited state in $B_9H_{13}.L$ (where L is pyridine itself or a pyridine substituted in the ring) there is an interaction between the π-electron orbital of the pyridine ring and the open three-centre bond B–B–B (p-orbitals) of the B_9H_{13} molecule: the excitation energy depends linearly on the Hammett constant (σ) in the pyridine series. A compound of the $B_9H_{13}.L$ type (where L is a neutral molecule, a donor of electrons) form a unique class of complex compound united by the properties of compounds with infra- and inter-molecular exchange of charges.

Muetterties and Aftandilian[209] obtained a compound of yet another type of nonaborane derivative, $B_9H_{14}P(C_6H_5)_2$ (however, the problem of the composition of the fragment has not been settled conclusively) by the alkaline hydrolysis of $B_{10}H_{13}P(C_6H_5)_2$ in alcoholic medium:

$$B_{10}H_{13}P(C_6H_5)_2 + 3H_2O \rightarrow B_9H_{14}P(C_6H_5)_2 + B(OH)_3 + H_2O.$$

A few salts of the anion $B_9H_{14}^-$ – with the cations Cs^+, $(CH_3)_4N^+$, and $(CH_3)_3\overset{+}{N}H$ – have been obtained[210] in the hydrolysis of $B_{10}H_{14}$ by aqueous bases; the salts were isolated and the anion characterised. Several reciprocal conversions of the compounds $B_9H_{13}.L$ and $X^+B_9H_{14}^-$ have been made, which confirm the structural similarity of these types of molecule.

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The boron hydrides are extremely reactive compounds, capable of various types of chemical reaction depending on the types of bond in them. Boron hydride chemistry is now developing very intensively both as regards the study of compounds already known and also in the preparation and study of new representatives of this class. The theory of the chemical structure of the boron hydrides still requires greater precision as the geometry of some boron hydrides and their NMR spectra have not been completely explained.

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NOTE ADDED IN PROOF

After submission of this paper for publication several review articles and collections of papers were published: Adams[211] dealt with the chemistry of the boron hydrides, Schaeffer[212] with the NMR spectra, Campbell[213] with structure, and Levinskass[214] with the toxicity of boron hydrides; new boron hydrides were also obtained: the anion $B_6H_6^{2-}$, octaborane(18) B_8H_{18},[216] and iso-nonaborane iso-B_9H_{15}.[217] Furthermore, articles have appeared on individual questions of boron hydride chemistry: on triborane[218], tetraborane[218-224], pentaboranes[225-229], hexaboranes[215,230-232], octaboranes[196,230,231,233], and nonaboranes[196,227,234].

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COVALENT ORGANODIELEMENTARY COMPOUNDS

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I. INTRODUCTION

Among organodielementary compounds we include compounds containing, apart from the usual elements (C, H, O, N, Cl, etc.), two inorganic elements. When the latter are metals, the compounds will be termed organodimetallic compounds.

In organodielementary compounds the inorganic elements may be separated by hydrocarbon groups or may be adjacent to one another. In the latter case the bond between them may be either ionic or covalent. Razuvaev and his coworkers are playing an active part in developing methods for the synthesis of organodielementary compounds having a covalent bond between the inorganic elements and also in examining their reactivity. The present paper reviews work in this field and is based on the literature up to May 1965. Investigations on organodielementary compounds having an ionic bond between the inorganic elements have been discussed several times in reviews and monographs [1-5].

II. METHODS OF PREPARATION

Organodielementary compounds containing an M–M' bond (here and below M and M' denote the inorganic elements) are usually prepared by reaction of R_3SiLi and analogous compounds with inorganic or organoelementary halides (method A), e.g.

$$(C_6H_5)_3SiK + (C_6H_5)_3SnCl \longrightarrow KCl + (C_6H_5)_3SiSn(C_6H_5)_3, \quad (1)$$

$$3(C_6H_5)_3GeNa + SiHCl_3 \longrightarrow [(C_6H_5)_3Ge]_3SiH + 3NaCl. \quad (2)$$

The yield of triphenyltriphenylsilyltin from reaction (1) is 76%;[6] tristriphenylgermylsilane is formed in quantitative yield in conformity with Eqn. (2).[7]

Method A has been used to synthesise several compounds containing Si–Ge,[6,8-12] Si–Sn,[7,13-16] Ge–Sn[17,18], Ge–Pb[18], and Sn–Pb[18] groups. Covalent organotrielementary compounds have been obtained in a similar manner[1]:

$$[(C_6H_5)_3Ge]_3SiLi + ClSn(C_6H_5)_3 \longrightarrow [(C_6H_5)_3Ge]_3SiSn(C_6H_5)_3 + LiCl.$$

In 1964 this method was used to synthesise a series of organodimetallic compounds having a neopentane configuration of metal atoms [18-21]:

$$4(C_6H_5)_3MLi + M'Cl_4 \longrightarrow [(C_6H_5)_3M]_4M' + 4LiCl,$$

$$4(C_6H_5)_3MLi + 2PbCl_2 \longrightarrow [(C_6H_5)_3M]_4Pb + Pb + 4LiCl,$$

where M = Pb, Sn and M' = Sn, Ge.

The attempt to obtain tetrakistriphenylgermyltin from triphenylgermyl-lithium and tin tetrachloride was unsuccessful[18], since in this case metal–halogen exchange predominates, with the formation of hexaphenyldigermane:

$$(C_6H_5)_3GeLi + SnCl_4 \longrightarrow (C_6H_5)_3GeCl + [LiSnCl_3],$$

$$(C_6H_5)_3GeCl + (C_6H_5)_3GeLi \longrightarrow LiCl + (C_6H_5)_6Ge_2.$$

This work showed that, in the synthesis of compounds of the type $[(C_6H_5)_3M]_4M'$ the tendency for metal–halogen exchange to occur diminishes in the sequence

$$(C_6H_5)_3GeLi > (C_6H_5)_3SnLi > (C_6H_5)_3PbLi.$$

The occurrence of this secondary process, which often leads to the formation of difficultly separable mixtures of products[8,17], is a substantial disadvantage of method A. Thus the interaction of $(C_6H_5)_3GeK$ with $(C_6H_5)_3SiCl$, for example, yields a difficultly separable mixture containing $(C_6H_5)_6Ge_2$, $(C_6H_5)_6Si_2$, and $(C_6H_5)_3GeSi(C_6H_5)_3$.[8,17] The attempt to prepare $(C_6H_5)_3SnSi(CH_3)_3$ from $(CH_3)_3SiCl$ and $(C_6H_5)_3SnLi$ failed, since in this system metal–halogen exchange and its accompanying processes occur preferentially[14]:

$$(C_6H_5)_3SnLi + (CH_3)_3SiCl \longrightarrow (C_6H_5)_3SnCl + (CH_3)_3SiLi,$$

$$(C_6H_5)_2SnCl + (C_6H_5)_3SnLi \longrightarrow LiCl + (C_6H_5)_6Sn_2 \text{ (yield 69\%)},$$

$$(CH_3)_3SiLi + (CH_3)_3SiCl \longrightarrow LiCl + (CH_3)_6Si_2.$$

Blake et al. have made the interesting observation that the interaction of $(CH_3)_3SiCl$ with $(C_4H_9)_3SnLi$ is preceded by dissociation of the latter compound[22]:

$$(C_4H_9)_3SnLi \rightleftarrows (C_4H_9)_2Sn + C_4H_9Li,$$

$$C_4H_9Li + (CH_3)_3SiCl \longrightarrow LiCl + (CH_3)_3SiC_4H_9,$$

the yield of butyltrimethylsilane being 54%. Such a process is not characteristic of the reaction of triphenylstannyl-lithium with triphenylchlorosilane[14].

Method A has been employed also for the synthesis of organodielementary compounds containing Si–Hg bonds. Attempts to use the reaction of triphenylsilyl-lithium with mercury halides, phenylmercuric chloride, or diphenylmercury were unsuccessful[23]. It was therefore supposed

that the Si–Hg bond in organosilicon compounds of mercury was unstable. This conclusion was subsequently disproved by the work of Wiberg [15], Razuvaev [24,25], and their coworkers. Wiberg, in particular, synthesised by method A triphenylsilyl derivatives of mercury, zinc, and aluminium:

$$n\,(C_6H_5)_3SiK + MCl_n \longrightarrow [(C_6H_5)_3Si]_nM + n\,KCl,$$

where M = Hg, Zn, Al and n = 2, 3. He showed also that interaction of R_3SnLi with chlorotrimethylsilane or a dialkyldichlorosilane in ether at -20° gives yields of up to 60–70% of compounds of types $R_3SnSi(CH_3)_3$ and $(R_3Sn)_2SiR'_2$, where R = C_2H_5, C_4H_9, C_6H_5 and R' = CH_3, C_6H_5.

The method was further developed by Schumann and Schmidt [26], who achieved the reaction

$$3\,(C_6H_5)_3SnLi + MCl_3 \longrightarrow [(C_6H_5)_3Sn]_3M + 3LiCl,$$

where M = As, Sb, Bi. The yield of the required products is ~80%. The chloride MCl_3 can be replaced by mixed organometallic compounds R_2MCl. In this way these workers obtained compounds containing one Sn–As covalent bond. The first representative of this class of compounds, diphenyltrimethylstannylarsine, had been obtained previously by a different method [27]. For the synthesis of compounds of the $R_3SnM(C_6H_5)_2$ series, where R = CH_3, C_2H_5, C_3H_7, C_4H_9 and M = As, Sb, see also Ref. 28. The infrared spectra of compounds containing covalent Sn–As and Sn–Sb bonds are discussed in Ref. 29.

Repeated attempts have been made to use method A [23,30] for the synthesis of compounds containing an Si–Bi, Si–Hg, Si–Cd, or Si–Zn bond. The reactions of triphenylsilyl--lithium with metal halides have been studied for this purpose. In the $(C_6H_5)_3SiLi$–$BiCl_3$ system the predominant reaction is metal–halogen exchange, leading to the formation of hexaphenyldisilane [30]. In some cases, nevertheless, the intermediate formation of organodielementary compounds is assumed [23] (e.g. in the reactions with mercury, lead, and tin halides). For the occurrence of unstable compounds containing an Si–P, Si–As, or Si–Sb bond in the reactions of triphenylsilyl-lithium with halides of Group V elements see Ref. 31.

Method A has been employed also for the synthesis of organodielementary compounds containing an Sn–P [32–34], Sn–Ti [35], Sn–B [36], or Pb–Ti [35] bond. There is no doubt that its synthetic possibilities have not yet been completely exhausted.

In 1963 Razuvaev and his coworkers began to apply the reaction of alkylated hydrides of Group IV elements with organometallic compounds to the synthesis of compounds containing covalent M–M'–M bonds (method B) [24,25,37–44]. The yield of organodielementary compounds is usually high:

$$n\,(C_2H_5)_3MH + (C_2H_5)_nM' \longrightarrow n\,C_2H_6 + [(C_2H_5)_3M]_nM',$$

where

M=Ge, Si;	M'=Hg, Cd, Zn;	n=2
M=Ge, Sn;	M'=Se;	n=2
M=Ge, Si;	M'=Tl;	n=3
M=Ge, Si, Sn;	M'=Bi, Sb;	n=3

Bistriethylgermylmercury was obtained at the same time, independently, and by the same reaction by Neumann and Kühlein [45]. These workers established [46,47], however, that method B can be used to synthesise complicated organodielementary compounds containing chains of inorganic elements, e.g.

$$4\,(C_6H_5)_2GeH_2 + 4\,(C_2H_5)_2Hg \longrightarrow 8C_2H_6 + 4/n\,[-(C_6H_5)_2GeHg-]_n \xrightarrow{h\nu} [(C_6H_5)_2Ge]_4 + [(C_6H_5)_2Ge]_n + 4Hg. \quad (3)$$

In 1964 method B was employed for the synthesis of bistriphenylstannyl sulphide [48]:

$$2\,(C_6H_5)_3SnH + (C_6H_5CH_2)_2S \longrightarrow 2C_6H_5CH_3 + [(C_6H_5)_3Sn]_2S.$$

Vyazankin et al. found that triethylsilane [24] and pentaethyldisilane [25] react with diethylmercury to form mainly products containing Si–Hg–C groupings:

$$R\,(C_2H_5)_2SiH + (C_2H_5)_2Hg \longrightarrow C_2H_6 + R\,(C_2H_5)_2SiHgC_2H_5, \quad (4)$$

where R = C_2H_5, $(C_2H_5)_3Si$. The yield of the symmetrical products — bistriethylsilylmercury and bis(pentaethyldisilanyl)mercury — was only 3.3% and 8.1% respectively. This has permitted the synthesis of triethylgermyl(triethylsilyl)mercury (26.2%) and of pentaethyldisilanyl(triethylgermyl)mercury (50.4%), which are the first organotrielementary compounds containing an Si–Hg grouping:

$$(C_2H_5)_3GeH + C_2H_5HgR \longrightarrow C_2H_6 + (C_2H_5)_3GeHgR, \quad (5)$$

where R = $(C_2H_5)_3Si$, $(C_2H_5)_3SiSi(C_2H_5)_2$.

It follows from Eqns. (4) and (5) that triethylgermane is more reactive than triethylsilane. This is confirmed by reactions (6)–(8), which constitute a further development of method B and from which it can be concluded that the reactivity of the hydrides in the above processes decreases in the sequence

$$(C_2H_5)_3SnH > (C_2H_5)_3GeH > (C_6H_5)_3SiH > (C_3H_7)_3SiH \simeq (C_2H_5)_3SiH\ [44]:$$

$$(C_2H_5)_3SnH + [(C_2H_5)_3Ge]_3M' \longrightarrow (C_2H_5)_3GeH + [(C_2H_5)_3Sn]_3M', \quad (6)$$

$$(C_2H_5)_3GeH + [(C_2H_5)_3Si]_3M' \longrightarrow (C_2H_5)_3SiH + [(C_2H_5)_3Ge]_3M', \quad (7)$$

$$(C_6H_5)_3SiH + [(C_2H_5)_3Si]_3M' \rightarrow (C_2H_5)_3SiH + [(C_6H_5)_3Si]_3M', \quad (8)$$

where M' = Bi, Sb.

Reaction (8) does not go to completion even under very severe conditions (230° for 20 h). The yield of hydrides and of the corresponding organodimetallic compounds in conformity with Eqns. (6) and (7) is quantitative.

In a study of the reaction of triethylgermane with triethylbismuth, Kruglaya et al. [42] established that, depending on the relative proportions of the starting materials, method B can be used to obtain not only $[(C_2H_5)_3Ge]_3Bi$ but also products of the partial replacement of ethyl by triethylgermyl groups:

$$n\,(C_2H_5)_3GeH + (C_2H_5)_3Bi \longrightarrow n\,C_2H_6 + [(C_2H_5)_3Ge]_nBi\,(C_2H_5)_{3-n},$$

where n = 1–3.

Method B has not yet been further developed on these lines. Nevertheless, this method has certain limitations. Thus compounds containing Sn–Cd, Sn–Tl, Sn–Zn [41], and Sn–Hg [24,25] bonds cannot be obtained in this way. It may merely be supposed that compounds of this type are intermediates in the reaction of $(C_2H_5)_3SnH$ with ethyl derivatives of cadmium, thallium, zinc, and mercury, since ethane and hexaethyldistannane are formed in high yield in all these cases, e.g. [24,25]

$$2\,(C_2H_5)_3SnH + (C_2H_5)_2Hg \longrightarrow 2C_2H_6 + [(C_2H_5)_3Sn]_2Hg \xrightarrow{} (C_2H_5)_6Sn_2 + Hg$$

Method B has not yet been widely used with success for the synthesis of substances containing M–M′ groupings, where M and M′ are elements of the silicon subgroup. However, there are grounds for assuming[49] that this limitation can be overcome:

$$(C_6H_5)_3GeH + (C_4H_9)_3SnN(C_2H_5)_2 \longrightarrow (C_2H_5)_2NH + (C_4H_9)_3SnGe(C_6H_5)_3.$$

In spite of the above disadvantages, this is undoubtedly a general method. In particular, method B can be used to obtain organodielementary compounds containing an ionic bond between the inorganic elements as well as those in which the bond is covalent. The metallation of organogermanium hydrides by organolithium compounds in tetrahydrofuran medium is well known[2,12,50]. In some cases, e.g. in the reaction of triphenylgermane with butyl-lithium, the yield is quantitative:

$$(C_6H_5)_3GeH + C_4H_9Li \longrightarrow C_4H_{10} + (C_6H_5)_3GeLi. \quad (9)$$

Discussing this reaction, Gilman[50] indicates, not without justification, that it is analogous to corresponding reactions of diphenylphosphine and of triphenylmethane[51,52]:

$$(C_6H_5)_2PH + C_4H_9Li \longrightarrow C_4H_{10} + (C_6H_5)_2PLi^{[51,52]},$$

$$(C_6H_5)_3CH + C_4H_9Li \longrightarrow C_4H_{10} + (C_6H_5)_3CLi^{[53,54]}.$$

Compounds containing Sn–Li[55], As–Li[56], P–Mg[57], and Sb–Li[58] ionic bonds have been prepared in a similar manner.

Recently, after a series of unsuccessful attempts[50], $(C_6H_5)_3GeMgCl$ has been prepared by the reaction of triphenylgermane with allylmagnesium chloride in tetrahydrofuran[59]. Finally, reports have recently appeared of the use of method B for the synthesis of compounds containing Ge–P [54], Sn–P [60], and Sn–As[60] bonds:

$$(C_6H_5)_2PH + (C_2H_5)_3GeN(CH_3)_2 \longrightarrow (CH_3)_2NH + (C_2H_5)_3GeP(C_6H_5)_2,$$

$$(C_6H_5)_2MH + R_3SnN(CH_3)_2 \longrightarrow (CH_3)_2NH + R_3SnM(C_6H_5)_2,$$

where M = P, As and R = CH_3, C_2H_5.

Besides the general methods A and B, several less developed routes are known for the synthesis of organodielementary compounds of the type under discussion. Thus triethyltriethylsilylgermane was obtained in 1963, for example, by the action of sodium on a mixture of bromotriethylsilane and bromotriethylgermane in the absence of solvents[61]; symmetrical products, containing Si–Si and Ge–Ge bonds, are formed at the same time.

Wiberg et al. [15], in an endeavour to use the Wurtz reaction to obtain compounds containing an Si–Si bond, studied the action of liquid sodium amalgam on halogenotrimethylsilanes. This led them to the synthesis of bistrimethylsilylmercury:

$$2(CH_3)_3SiX + 2Na + Hg \rightarrow [(CH_3)_3Si]_2Hg + 2NaX,$$

where X = Cl, Br. The compounds $Hg[Si(CH_3)_{3-n}H_n]_2$, where n = 1, 2, could not be obtained by the action of sodium amalgam on methylbromosilanes, but there is no doubt that they are formed as intermediates in this process.

Several original methods were developed during 1963–1964 for the preparation of compounds containing Pb–S [62], Sn–Se [63,64], Sn–Te [63,64], Sn–S–Pb[65], Sn–S [63,66], Ge–S [67], and Si–Sb[68] bonds.

Organodimetallic and organopolymetallic compounds having covalent bonds between transition metals and metals of Group IV*b* have been investigated intensively during recent years. The possibility of preparing compounds of this type was first reported by Hein and his coworkers[69]: by the action of organolead hydroxides on $Ca[HFe(CO)_4]_2$ they obtained two types of compounds containing a covalent Pb–Fe bond – $[Alk_2PbFe(CO)_4]_2$ and $(R_3Pb)_2Fe(CO)_4$, where R represents phenyl or cyclohexyl.

A method based on the reactions of salts of hydrocarbonyls with organometallic halides of Group IV*b*, e.g. [70]

$$R_{4-n}SnCl_n + n\,Na[Co(CO)_4] \longrightarrow n\,NaCl + R_{4-n}Sn[Co(CO)_4]_n,$$

where n = 1,2 and R = CH_3, C_4H_9, proved to be more generally applicable. The compounds $(C_4H_9)_2SnFe(CO)_4$,[70] $[(C_6H_5)_2PbFe(CO)_4]_2$,[71] $C_5H_5Fe(CO)_2Si(CH_3)_3$,[72,73] $(C_6H_5)_3GeMn(CO)_5$,[74] and $(C_6H_5)_3GeFe(CO)_2C_5H_5$ [74] have been obtained in this way. Gorsich[75] used the same method to synthesise compounds containing covalent Sn–Mn, Pb–Mn, and Sn–Fe bonds.

In recent years two further methods have been worked out for the preparation of compounds containing an Sn–Fe bond. Compounds of the type $[R_2SnFe(CO)_4]_2$, where R = CH_3, C_4H_9, have been obtained in low yields by the interaction of pentacarbonyliron and $R_2Sn(C_6H_5)_2$ in boiling ethylcyclohexane[76]. The second method is based on the reaction[77]

$$[C_5H_5Fe(CO)_2]_2 + SnCl_2 \longrightarrow [C_5H_5Fe(CO)_2]_2SnCl_2 \xrightarrow{+2C_2H_5MgBr} [C_5H_5Fe(CO)_2]_2Sn(C_2H_5)_2. \quad (A)$$

The compound A has also been synthesised by the reaction

$$2C_5H_5Fe(CO)_2Na + Cl_2Sn(C_2H_5)_2 \longrightarrow 2NaCl + A.$$

In 1964 Nesmeyanov and his coworkers prepared organodimetallic compounds containing Re–M, Mo–M, and W–M bonds, where M = Sn, Pb, by the reaction of organometallic chlorides with $NaRe(CO)_5$,[78] $NaMo(CO)_3C_5H_5$, $NaW(CO)_3C_5H_5$, and $NaCr(CO)_3C_5H_5$.[79]

Quite recently these workers[80] have obtained new polymetallic compounds of tin with carbonyls of metals in Groups VI–VIII by the reactions

$$(CO)_5MnSn(C_6H_5)_2Cl + NaM(CO)_n \longrightarrow (CO)_5MnSn(C_6H_5)_2M(CO)_n, \quad (M = Co, Re)$$

$$(CO)_5MnSn(C_6H_5)_2Cl + NaM'(CO)_3C_5H_5 \longrightarrow (CO)_5MnSn(C_6H_5)_2M'(CO)_3C_5H_5. \quad (M' = Mo, W)$$

The elaboration of methods for the synthesis of the above compounds has been accompanied by an investigation of their structure and reactivity. As early as 1957 it was suggested[70] that the tin and cobalt atoms in the compound $(C_4H_9)_2Sn[Co(CO)_3P(C_6H_5)_3]_2$ were linked indirectly through carbonyl groups. The view was also expressed[72,75] that the metal atoms were joined by a covalent bond in these compounds. In 1964 Bryan[81] studied the crystal structure of $(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$, and found that the Sn, Mn, and P atoms are collinear and are linked covalently. X-Ray examination[79] of $C_5H_5(CO)_3Mo–Sn(C_6H_5)_3$ also confirms the presence of a σ-bond between molybdenum and tin atoms.

The reactivity of these compounds is determined by the nature of the atoms forming the metal–metal bond. Some of the compounds (e.g. those containing Sn–Co[70], Fe–Si[72], Fe–Sn[76], Pb–Mn[75], and Sn–Mn[75] bonds) tend to undergo oxidation, and are prepared in an atmosphere of nitrogen. In contrast, compounds containing Cr–M, Mo–M, and

W–M bonds, where M = Sn, Pb[79], and also Sn–Re, Pb–Re[78], are quite stable.

Chlorine, bromine, and hydrogen chloride do not cleave Sn–Mn[75] and Sn–Re[78] bonds. They do cleave an Sn–C bond[75,78,79]:

$$(C_6H_5)_3SnMn(CO)_5 + 3Cl_2 \longrightarrow Cl_3SnMn(CO)_5 + 3C_6H_5Cl,$$
$$(C_6H_5)_3SnRe(CO)_5 + 2Br_2 \longrightarrow (C_6H_5)Br_2SnRe(CO)_5 + 2C_6H_5Br,$$
$$(C_6H_5)_3SnMo(CO)_3C_5H_5 + 2HCl \longrightarrow (C_6H_5)Cl_2SnMo(CO)_3C_5H_5 + 2C_6H_6.$$

Hydrogen chloride has a similar effect on $(C_6H_5)_3SnW(CO)_3(C_5H_5)$, $(C_6H_5)_2Sn[Mo(CO)_3C_5H_5]_2$, $(C_6H_5)_2Sn[W(CO)_3C_5H_5]_2$, and $(C_6H_5)_3SnFe(CO)_2C_5H_5$.[77,79]

According to Gorsich[75] pentacarbonyltriphenylstannylmanganese, like simple metal carbonyls[3], reacts with triphenylphosphine and triphenylarsine, a molecule of carbon monoxide being displaced. The resulting product (B) has been prepared also by an alternative synthesis:

$$(C_6H_5)_3SnMn(CO)_5 + P(C_6H_5)_3 \xrightarrow{-CO} (C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3 \quad (B)$$
$$(C_6H_5)_3SnCl + NaMn(CO)_4P(C_6H_5)_3 \xrightarrow{-NaCl} (C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3 \quad (B)$$

On treatment with chlorine in dichloromethane, compound (B) is converted into $Cl_3SnMn(CO)_4P(C_6H_5)_3$ in 64% yield.

III. PROPERTIES OF COMPOUNDS OF THE TYPE $(R_3M)_nM'$ (M = Si AND ITS ANALOGUES; M' = Hg, Cd, Sb, etc.)

Organodielementary compounds of the type $(R_3M)_nM'$ are very reactive and have very varied chemical properties. Unfortunately their structural analogues $(R_3C)_nM'$ have in general been little studied, and therefore it is impossible to make a precise comparison of the properties and reactivities of these two classes of compounds. Most of the chemical reactions which these compounds undergo involve cleavage of covalent M–M' bonds with preservation of the R_3M fragments.

1. Thermal and Photochemical Decomposition

In most compounds of the type $(R_3M)_nM'$ extraordinary reactivity is combined with great thermal stability. In the absence of atmospheric oxygen, tristriethylsilylantimony and all its isologues other than tristriethylstannylbismuth can be distilled in a vacuum without appreciable decomposition[44]. This property is possessed also by bistrimethylsilylmercury[15], bistriethylsilylmercury[24], and bistriethylgermylmercury[39]. The examples of $(C_2H_5)_3SiHgC_2H_5$, $(C_2H_5)_3SiSi(C_2H_5)_2HgC_2H_5$, $(C_2H_5)_3SiHgGe(C_2H_5)_3$, and $(C_2H_5)_3SiSi(C_2H_5)_2HgGe(C_2H_5)_3$ show that compounds containing Si–Hg–C, Si–Si–Hg–C, Si–Hg–Ge, and Si–Si–Hg–Ge groupings are more stable than the usual unsymmetrical organomercury compounds[24,25]. In spite of the complexity of their structure, they distil in a vacuum without decomposition or symmetrisation.

The thermal stability of compounds of the type $[(C_2H_5)_3M]_3M'$ is determined by the stability of the M–M' bonds, and diminishes in the sequence Si–Sb ≃ Ge–Sb > Si–Bi ≃ Ge–Bi > Sn–Sb > Sn–Bi > Ge–Tl [44]. The least stable compounds of this series break down according to the equation

$$2[(C_2H_5)_3M]_3M' \rightarrow 3(C_2H_5)_6M_2 + 2M', \quad (10)$$

where M = Ge, M' = Tl and M = Sn, M' = Bi; and of the $[(C_2H_5)_3M]_2M'$ series according to the equation

$$[(C_2H_5)_3M]_2M' \rightarrow (C_2H_5)_6M_2 + M', \quad (11)$$

where M = Si, Ge and M' = Cd. Bistrimethylsilylmercury decomposes in the same way[15].

Tristriethylsilylantimony decomposes at ~300° with the quantitative liberation of antimony and the formation of $(C_2H_5)_3Si^{\bullet}$ radicals. The latter abstract hydrogen from surrounding molecules, giving triethylsilane and a complicated mixture of high-boiling organosilicon compounds.

According to Eaborn and his coworkers[82] the decomposition of bistrimethylsilylmercury in solvents also goes by a free-radical mechanism. The trimethylsilyl radicals can dimerise, abstract hydrogen from toluene and other solvents, replace the methyl group in anisole, and undergo other elementary reactions.

The thermal breakdown of compounds of general formula $[(C_2H_5)_3M]_nM'$ usually involves, independently of its mechanism, quantitative separation of the metal M' in the free state[40,44]. The element M, on the other hand, remains combined even when $(C_2H_5)_3M$ fragments are subject to free-radical attack. Tristriethylstannylantimony is an exception, decomposing with partial separation of tin[44]. In the presence of 2–3 wt.% of $AlBr_3$ the decomposition of tristriethylstannylantimony and its bismuth analogue follows a quite different path, the reaction conforming exactly to the equation

$$4[(C_2H_5)_3Sn]_3M' \rightarrow 9(C_2H_5)_4Sn + 3Sn + 4M', \quad (12)$$

where M' = Sb, Bi. Compounds of the type of $AlCl_3$ have a similar effect on the mechanism of the thermal decomposition of hexaethyldistannane[83].

According to Wiberg the thermal breakdown of polymeric dimethylsilylenemercury, obtained by the action of sodium amalgam on dimethyldibromosilane[15], is accompanied by the separation of the free metal and the formation of Si–Si bonds:

$$[(CH_3)_2SiHg]_n \rightarrow nHg + [(CH_3)_2Si]_n.$$

Organosilicon and organogermanium compounds of mercury have proved very sensitive to the action of light, which has enabled Neumann[46,47] to use ultraviolet radiation to decompose a polymer containing a $[Ge–Hg]_n$ chain — see Eqn. (3).

Razuvaev and his coworkers have shown[39] that bistriethylgermylmercury, while possessing quite high thermal stability, readily undergoes photolysis

$$[(C_2H_5)_2Ge]_2 \cdot Hg \xrightarrow{h\nu} (C_2H_5)_6Ge_2 + Hg,$$

even if the ultraviolet radiation is filtered through molybdenum glass.

This process probably does not involve the formation of kinetically independent $(C_2H_5)_3Ge$ radicals, since, when it is conducted in cumene, tetraethyltin, or t-butyl peroxide, these compounds act as inert solvents. This hypothesis is consistent also with the fact that the photolysis of triethylgermyltriethylsilylmercury does not result in the formation of compounds containing Si–Si and Ge–Ge bonds, as

might have been expected if $(C_2H_5)_3Ge^{\bullet}$ and $(C_2H_5)_3Si^{\bullet}$ radicals had escaped "from the cage" into the bulk of the solution [25]:

$$(C_2H_5)_3GeHgSi(C_2H_5)_3 \xrightarrow{h\nu} Hg + (C_2H_5)_3GeSi(C_2H_5)_3.$$

All the above information on the decomposition of organodielementary compounds has been obtained in work with pure substances in the absence of atmospheric oxygen. The literature also contains data on the breakdown of several unstable organodielementary compounds in the course of their synthesis. In considering these results it must be borne in mind that the mechanism of the decomposition may be very different in the presence of foreign substances — cf. Eqns. (10) and (12).

Wiberg et al. [15], investigating the possibility of synthesising compounds of type $[Si(CH_3)_nH_{3-n}]_2Hg$ (n = 1, 2) by the action of sodium amalgam on methylbromosilanes, found that they break down in two ways in the process of preparation — (*a*) with the formation of disilanes $[Si(CH_3)_nH_{3-n}]_2$ by a reaction analogous to (11) and (*b*) with the formation of compounds $(CH_3)_nSiH_{4-n}$ and $(CH_3)_nSiH_{2-n}$ by the disproportionation of silicon-containing groups split off from the mercury.

When n = 3 reaction takes place solely by the first route, and when n = 1 solely by the second. When n = 2 both types of decomposition occur at the same time, but disproportionation processes predominate. These workers also studied the interaction of mercury dichloride with triphenylsilylpotassium in liquid ammonia, and showed that the bistriphenylsilylmercury formed decomposes to a considerable extent during the synthesis:

$$[(C_6H_5)_3Si]_2Hg \xrightarrow{a} (C_6H_5)_6Si_2 + Hg$$
$$[(C_6H_5)_3Si]_2Hg \xrightarrow{b} Hg + (C_6H_5)_4Si + (C_6H_5)_2Si$$

Route (*b*), which represents a side-reaction in the decomposition of bistriphenylsilylmercury, is the main reaction in the thermolysis of bistriphenylsilylzinc and bistriphenylsilylbarium [15]. The diphenylsilene $(C_6H_5)_2Si$ which is thus formed is converted into phenylated polysilanes $(C_6H_5)_3Si[Si(C_6H_5)_2]_nSi(C_6H_5)_3$.

2. Reactions with Atmospheric Oxygen and with Peroxides

Compounds of the type $(R_3M)_nM'$ are readily oxidised, and react vigorously with organic peroxides. The reactions occur at room temperature with the evolution of heat. The oxidation of bistriethylgermylmercury [39,45] is accurately represented by the equation

$$2[(C_2H_5)_3Ge]_2Hg + O_2 \longrightarrow 2[(C_2H_5)_3Ge]_2O + 2Hg.$$

The reaction can be employed for the determination of mercury in a substance. Bistriphenylgermylmercury [45], bistriethylgermylcadmium [40], and bistriethylsilylmercury [24] are oxidised in a similar manner.

According to results obtained by Vyazankin et al. [24] the oxidation of ethyltriethylsilylmercury is preceded by its symmetrisation. As a result, the oxidation products are found to contain diethylmercury, metallic mercury, and hexaethyldisiloxane:

$$2(C_2H_5)_3SiHgC_2H_5 \longrightarrow (C_2H_5)_2Hg + [(C_2H_5)_3Si]_2Hg$$
$$[(C_2H_5)_3Si]_2Hg \xrightarrow{+\frac{1}{2}O_2} Hg + [(C_2H_5)_3Si]_2O$$

The reactions with acyl peroxides are represented by equally simple stoichiometric equations [24,39,44]:

$$[(C_2H_5)_3M]_2Hg + (C_6H_5COO)_2 \longrightarrow Hg + 2(C_2H_5)_3MOCOC_6H_5, \quad (13)$$

where M = Ge, Si; and

$$2[(C_2H_5)_3M]_3M' + 3(C_6H_5COO)_2 \longrightarrow 2M' + 6(C_2H_5)_3MOCOC_6H_5, \quad (14)$$

where M = Si, Ge, Sn and M′ = Sb, Bi.

Bistriethylgermylmercury reacts with dicyclohexyl peroxodicarbonate in a similar fashion, with a quantitative yield of mercury [25]:

$$[(C_2H_5)_3Ge]_2Hg + (C_6H_{11}OCOO)_2 \rightarrow Hg + 2(C_2H_5)_3GeOCOOC_6H_{11}.$$

The second product is unstable, and is readily decarboxylated with the formation of cyclohexyloxytriethylgermane.

When bistriethylgermylcadmium [40], its silicon analogue [43], and compounds containing Ge–Zn bonds [41] are treated with benzoyl peroxide, cadmium (zinc) benzoate is formed as well as $C_6H_5COOM(C_2H_5)_3$ (M = Ge, Si). Reduction of the central atom to the elementary state — cf. Eqns. (13) and (14) — does not take place. The reaction of tristriethylgermylthallium with benzoyl peroxide is represented by the equation

$$[(C_2H_5)_3Ge]_3Tl + 2(C_6H_5COO)_2 \rightarrow 3(C_2H_5)_3GeOCOC_6H_5 + TlOCOC_6H_5.$$

In the authors' opinion the reactions with acyl peroxides take place by a latent-radical mechanism with the intermediate formation of cyclic active complexes. This is consistent with the following facts:

1. The reactions of acyl peroxides with organodielementary compounds are exothermic. At 5–10° they are complete within a few minutes. Under these conditions the starting materials are severally stable, and do not initiate free-radical processes.

2. Free-radical reactions are usually complicated. They involve the formation of multicomponent mixtures, which does not occur in the present cases.

3. Dibromoethane (see below) reacts similarly to acyl peroxides with organodielementary compounds. Reactions with monobromo-derivatives, in which the formation of cyclic active complexes is improbable, take place only under the influence of heat or light.

The ability of organodielementary compounds to react with acyl peroxides under mild conditions is not a specific property of substances containing M–M′–M groupings: benzoyl peroxide reacts equally vigorously with ethyltriethylsilylmercury, which contains a single Si–Hg bond [24]. Finally, the earlier papers of Razuvaev, Vyazankin, and their collaborators showed that acyl peroxides react at ~20° with hexaethyldistannane [83–85], diethyltin [37] (the polymeric nature of which has recently been rigorously proved [86]), and also with substances containing branched chains of tin atoms [85,87], by smoothly cleaving the Sn–Sn bonds. Polymeric diphenyltin reacts with benzoyl peroxide with the partial rupture of Sn–Sn bonds [88].

The Si–Si bond in hexaethyldisilane, on the other hand, is not cleaved by acyl peroxides even under conditions such that the latter break down, when the reaction aquires a free-radical character [83] and shows great complexity.

In contrast to acyl peroxides, t-butyl peroxide does not react with organodielementary compounds at room temperature. Moreover, as has been stated above, under mild conditions it is possible to accomplish the photodecomposition of bistriethylgermylmercury without affecting the t-butyl peroxide [24]. This is probably the first case

of a homolytic process in which a peroxy-compound acts as an inert solvent.

3. Reactions with Halogenated Derivatives

The photochemical reactions of halogeno-derivatives with ordinary organometallic compounds containing a single metal atom have been investigated in detail and discussed by Razuvaev and his coworkers [89-91]. The reactions usually occur by a free-radical mechanism:

$$R_nM \xrightarrow{h\nu} R_{n-1}M^{\cdot} + R^{\cdot},$$
$$R_{n-1}M^{\cdot} + R'X \longrightarrow R_{n-1}MX + R',$$

where R and R′ are aliphatic or aromatic groups, M is an n-valent metal, and X = Cl, Br, more rarely I. The fate of the radicals R and R′ which are formed is determined by their structure, also by the nature of the halogeno-derivative R′X, and by the properties of the initial organometallic compound R_nM.

The photochemical reactions of alkyl halides with organodielementary compounds follow a quite different scheme, e.g. [24,39]

$$[(C_2H_5)_3Ge]_2Hg + 2RBr \xrightarrow{h\nu} 2(C_2H_5)_3GeBr + R_2Hg,$$

where R = C_2H_5, C_6H_5, $C_6H_5CH_2$, 1-$C_{10}H_7$. The authors assume these reactions to occur "in a cage" with homolytic cleavage of C–Br and Ge–Hg bonds. Alkyl bromides react in a similar way with compounds of type $[(C_2H_5)_3M]_3Sb$ on heating [44]:

$$[(C_2H_5)_3M]_3Sb + 3RBr \longrightarrow 3(C_2H_5)_3MBr + R_3Sb,$$

where M = Sn, Ge; R = $C_6H_5CH_2$, cyclo-C_5H_9. The yields of the compounds R_3Sb vary from 57% to 75%. Finally, the reaction of bistriethylsilylcadmium with ethyl bromide (~80° for 2 h) yields bromotriethylsilane (36%) and diethylcadmium (76%). [43] Under comparable conditions bistriethylgermylcadmium [40] reacts with alkyl bromides by a different, more usual route:

$$[(C_2H_5)_3Ge]_2Cd + 2RBr \rightarrow CdBr_2 + 2(C_2H_5)_3GeR,$$

where R = C_2H_5, $C_6H_5CH_2$.

Bisdibutylstibylmagnesium reacts similarly with allyl bromide, the products being allyldibutylantimony (31%) and magnesium bromide [68]. The reaction of ethyl bromide with compounds containing Ge–Zn bonds also proceeds "normally", with the formation of $ZnBr_2$ and $R_3GeC_2H_5$. [41]

A very characteristic reaction of organodielementary compounds containing M–M′–M groupings is that with 1,2-dibromoethane, which is exothermic and is complete at room temperature within a few minutes, e.g. [42]

$$[(C_2H_5)_3Ge]_2Hg + CH_2BrCH_2Br \rightarrow 2(C_2H_5)_3GeBr + Hg + C_2H_4.$$

The yields of mercury, ethylene, and bromotriethylgermane are respectively 97%, 75%, and 58%. Tristriethylsilylantimony reacts similarly with excess of dibromoethane [44]. With equimolecular proportions of the reactants, ethylene and bromotriethylsilane are formed together with a viscous, coloured, readily oxidisable substance, which is regarded as polymeric triethylsilylantimony:

$$n[(C_2H_5)_3Si]_3Sb + nCH_2BrCH_2Br \rightarrow nC_2H_4 + 2n(C_2H_5)_3SiBr + [(C_2H_5)_3SiSb]_n.$$

This hypothesis is consistent with the reactions of (cyclo-$C_6H_{11})_2SbLi$ [58] and $C_6H_5AsLi_2$ [92] with dibromoethane, in the course of which Sb–Sb and As–As bonds are formed. The products are tetracyclohexyldistibine and arsenobenzene, together with ethylene and lithium bromide.

The reaction of dibromoethane with bistriethylgermylcadmium [40] differs somewhat from those considered above. In this case the central atom (cadmium) is not reduced to the free metal. The reaction products are cadmium bromide (74%), ethylene (73%), and bromotriethylgermane (86%). In the reaction between dibromoethane and tristriethylgermylthallium the thallium passes from the tervalent to the univalent state:

$$[(C_2H_5)_3Ge]_3Tl + 2CH_2BrCH_2Br \rightarrow 2C_2H_4 + 3(C_2H_5)_3GeBr + TlBr.$$

4. Reactions with Metals and Their Salts

The reactions with metals of ordinary organometallic compounds (containing a single metal atom), accompanied by the transfer of radicals from one metal to the other, have been investigated in detail and are widely employed for synthetic purposes. The first attempt to transfer a trimethylsilyl radical from metal to metal (from mercury to zinc and aluminium) was undertaken by Wiberg et al. [15] They showed that, when bistrimethylsilylmercury reacts with zinc, which occurs only at high temperatures, the mercury is not replaced by zinc but dimethylmercury is formed. The mechanism of the process was not discussed. Reaction of bistrimethylsilylmercury with activated aluminium takes place at a more moderate temperature (80°) with the quantitative separation of mercury and a mixture of products containing no Si–Al bonds.

In the authors' opinion this is explained by the instability of the $>Al-Si(CH_3)_3$ groups in the tristrimethylsilylaluminium formed as intermediate:

$$[(CH_3)_3Si]_3Al \rightarrow Al(CH_3)_3 + 3(CH_3)_3Si.$$

This is followed by "saturation" of the dimethylsilene by the $(CH_3)_3Si$ groups of the bistrimethylsilylmercury, with the production of polysilanes of the $(CH_3)_3Si[Si(CH_3)_2]_nSi.(CH_3)_3$ series. In an investigation of the same problem Vyazankin et al. [93] showed that at 50° metallic mercury displaces cadmium from diethylcadmium, bistriethylsilylcadmium, and its germanium analogue:

$$Hg + R_2Cd \rightarrow Cd + R_2Hg,$$

where R = C_2H_5, $(C_2H_5)_3Si$, $(C_2H_5)_3Ge$.

Mercury reacts more vigorously (within 1½ h at 20°) with tristriethylgermylthallium, the yield of bistriethylgermylmercury reaching 78%. The resulting mercury compound can in turn act as starting material for the synthesis of triethylgermyl-lithium and its sodium analogue in high yields:

$$[(C_2H_5)_3Ge]_2Hg + 2M \rightarrow Hg + (C_2H_5)_3GeM,$$

where M = Li, Na. The reaction goes readily in tetrahydrofuran medium.

Organodielementary compounds acts as reducing agents towards metal salts. Wiberg et al. found [15] that bistriphenylsilylbarium and bistriphenylsilylzinc reduce silver nitrate to metallic silver. Similar behaviour is shown by the compound containing Al–Si bonds obtained by the action of triphenylsilylpotassium on aluminium chloride in tetrahydrofuran.

According to Razuvaev and his coworkers [93] bistriethylgermylcadmium reacts with mercuric chloride to form mercury (71%), cadmium chloride (82%), and chlorotriethylgermane (31%), the reaction being exothermic. Metallic mercury is formed also by the interaction of mercuric chloride with compounds containing Ge–Zn–Ge groups [41].

5. Other Reactions

The interaction of organodielementary compounds with acids involves cleavage of the M–M′–M grouping, the central atom separating as the free metal, e.g. [42]

$$2\,[(C_2H_5)_3Ge]_3Bi + 3\,CH_3COOH \rightarrow 3\,(C_2H_5)_3GeOCOCH_3 + 3\,(C_2H_5)_3GeH + 2\,Bi,$$

Acetic acid reacts similarly with bistriethylgermylmercury [42] and with bistriethylgermylcadmium [93]. Bistrimethylsilylmercury reacts with hydrochloric acid [15] in the same way; the reaction is quantitative, and may serve as a method of analysis for mercury.

Under normal conditions bistriethylgermylmercury and its silicon analogue are stable to hydrolysis or alcoholysis even after many months of contact with water or alcohols. Bistriethylgermylcadmium [40,93], on the other hand, interacts with these reagents under mild conditions:

$$[(C_2H_5)_3Ge]_2Cd + RH \longrightarrow (C_2H_5)_3GeH + (C_2H_5)_3GeR + Cd,$$

where R = OH, n-C_3H_7O.

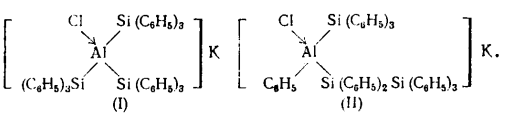
The hydrolysis of bistriphenylbarium with moist methanol proceeds differently [15]:

$$[(C_6H_5)_3Si]_2Ba + 4H_2O \longrightarrow Ba(OH)_2 + 2H_2 + 2\,(C_6H_5)_3SiOH.$$

In the authors' opinion the complex $KCl.Al[Si(C_6H_5)_3]_3$, which is the first organodielementary compound containing covalent Si–Al bonds, is hydrolysed by alcoholic potassium hydroxide in a similar manner. The fact that this involves the evolution of only two moles of hydrogen, not the three that might have been expected from the equation

$$KCl\cdot Al[Si(C_6H_5)_3]_3 + 6H_2O \longrightarrow KCl + Al(OH)_3 + 3\,(C_6H_5)_3SiOH + 3H_2,$$

led the authors to assign to the complex the structure (II) instead of (I)



(I) (II)

For the reaction of this substance with hydrochloric acid see Ref. 15.

Zinc hydroxide and triphenylsilane have been isolated from the hydrolysis of bistriphenylsilylzinc with dilute hydrochloric acid [15]. Compounds of the type $(C_2H_5)_3GeZn.[Ge(C_2H_5)_2]_nGe(C_2H_5)_3$, which are formed by the interaction of triethylgermane and diethylzinc, are hydrolysed in a similar manner [41].

IV. PROPERTIES OF COMPOUNDS OF TYPE $R_3M–M'R_3$ (WHERE M AND M′ ARE ELEMENTS OF GROUP IV*b*)

In comparison with the compounds described in the preceding Section, those of the $R_3M–M'R_3$ series, where M and M′ represent elements of the silicon subgroup, possess immeasurably smaller reactivity. The completely arylated compounds $(C_6H_5)_3SiGe(C_2H_5)_3$, [8] $(C_6H_5)_3SiSn(C_6H_5)_3$, [94] and $(C_6H_5)_3GeSn(C_6H_5)_3$ [17] are closely similar in chemical properties to hexaphenyldisilane and its analogues, and differ sharply from hexaphenylethane in the absence of any tendency to dissociate into radicals. These compounds are stable to atmospheric oxygen, and are not cleaved by water, alcohols, or acids. In the fully phenylated compounds the Si–Ge bond is not ruptured by iodine in boiling chloroform or by organolithium compounds, whereas the Ge–Sn bond is unstable towards these reagents. According to Gilman and his coworkers, replacement of phenyl by alkyl groups in compounds of this type leads to a strengthening of the M–M′ bonds.

Metals of the lithium subgroup and their alloys are extremely effective agents for the cleavage of M–M′ bonds. Correct choice of solvent is extremely important for the successful conduct of the reactions. Triphenyltriphenylsilylgermane is cleaved by a sodium–potassium alloy in ether [8]. In the case of triphenyltriphenylstannylgermane this alloy is effective only in tetrahydrofuran [17]. Trimethyltriphenylsilyltin is split by sodium in liquid ammonia [95]. Triphenyltriethylsilylgermane is cleaved at the Si–Ge bond by lithium in triethylamine [10]. Aliphatic derivatives containing Si–Ge [61] and Si–Sn [15] bonds have recently been synthesised, but very little work has been done on their chemical properties. It has been established that stannylsilanes of the types $R_3SnSiR'_3$ and $(R_3Sn)_2SiR'_2$ (where R = C_2H_5, C_4H_9, C_6H_5, and R′ = CH_3, C_6H_5) are stable in air. They undergo an exothermic reaction with $TiCl_4$, reducing it to $TiCl_3$. The latter can be isolated from the mixture in a polymerisation-active state [15].

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This review makes it plain that three types of organodielementary compounds containing covalent M–M′ bonds exist. Compounds in which M and M′ are elements of the silicon subgroup belong to the least varied type. Representatives of this group are the least reactive. Substances containing M–M′–M groups (M = Si and its analogues and M′ = Hg, Cd, Al, Bi, etc.), on the other hand, are highly reactive, and their properties are extremely unusual.

The third type of compounds, which has been studied intensively, contains metal–transition metal bonds. The striking features of compounds of this type are their variety and the unexpected stability of the M–M′ groupings.

All the compounds which have been described are of great interest for study of the nature of the chemical bond in general and of the metal–metal bond in particular. As research develops, they will undoubtedly also find practical application.

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STEREOCHEMISTRY OF ORGANIC COMPOUNDS OF PHOSPHORUS AND ARSENIC

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I. INTRODUCTION

Acquaintance with the world's chemical literature must lead to the conclusion that interest has grown appreciably during recent years in problems of the stereochemistry not only of carbon compounds but also of those of other elements — nitrogen, phosphorus, sulphur, arsenic, antimony, etc. — in the Periodic System. The reason for the increasing number of stereochemical investigations is undoubtedly that this field, which until not long ago was regarded as one of the most abstract, is beginning to acquire ever increasing practical importance. Stereochemical features of structure have a great influence on the biochemical properties of organic compounds. Knowledge of the configurational relationships among various types of optically active compounds is of practical and theoretical importance. It is required in many fields of biochemistry for the study of metabolism and the action of drugs, in working out theoretical problems of biogenesis, etc. The use of optically active reactants often considerably facilitates study of the mechanism of chemical reactions. A systematic study of the stereochemistry of reactions will inevitably lead in the future to a more profound understanding of the chemical changes occurring in living Nature.

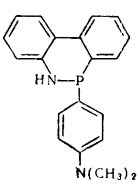
Interest has grown considerably during recent years in the stereochemistry of organic compounds of phosphorus and arsenic, especially the former. The first attempts to obtain optically active compounds containing asymmetric phosphorus and arsenic atoms were made at the beginning of the present century. In 1911 Meisenheimer[1,2] showed for the first time, with ethylmethylphenylphosphine oxide as example, that phosphorus can act as an asymmetric centre in a molecule. The first optically active organic compound of arsenic — the dextrorotatory benzylmethyl--1-naphthylphenylarsonium iodide — was obtained in 1921 by Burrows and Turner[3].

A. Michaelis, J. Meisenheimer, A. E. Arbuzov, B. A. Arbuzov, G. Kh. Kamai, D. M. Coyne, H. S. Aaron, L. Horner, J. Michalski, and many others have devoted their researches to the difficult but interesting field of the stereochemistry of organophosphorus and organoarsenic compounds, and definite progress has now been achieved.

II. STEREOCHEMISTRY OF ORGANIC COMPOUNDS OF TERVALENT PHOSPHORUS AND ARSENIC

The phosphorus atom has the electronic configuration $(1s^2)(2s^2)(2p^6)(3s^2)(3p^3)$, so that it can have covalencies of 3–6 in its compounds. Organic derivatives of tervalent phosphorus can be regarded as derivatives of phosphine PH_3 in which one, two, or three hydrogen atoms have been replaced by organic radicals. Phosphines have the configuration of a trigonal pyramid. This is evident from the fact that in the tervalent state phosphorus utilises only $3p$-electrons, as is confirmed by the valency angle of 94° in phosphine and 101 ± 3° in trimethylphosphine. Thus a tertiary phosphine $PR^1R^2R^3$ should exist in the form of two optical isomers, related to one another as an object to its mirror image. Until recently derivatives of tervalent phosphorus remained almost uninvestigated from the point of view of optical isomerism. The calculated frequency of oscillation of the phosphorus atom[4] is 5×10^6 s^{-1}. Calculations by Weston[5] showed on the basis of the oscillation frequency that the half-life (or rate of racemisation) for trimethylphosphine is 2 h at 7°. It appeared that optical isomers of asymmetric tertiary phosphines would be stable only at low temperatures. Until recently investigators adhered to this view, and in fact no-one attempted to resolve tertiary phosphines of the type $PR^1R^2R^3$ into optical isomers.

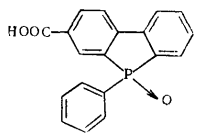
It was suggested that the stability of optical isomers of tervalent phosphorus compounds should be increased if the phosphorus atom formed part of a ring system, since oscillation of the phosphorus atom would then be impeded. Campbell and Way[6] have resolved the cyclic phosphine 10-*p*-dimethylaminophenyl-9,10-dihydro-9-aza-10-phosphaphenanthrene



into optical isomers by reducing the optically active isomeric oxides of this phosphine with lithium tetrahydroaluminate. The isolated isomers of the phosphine proved to have far greater optical stability than could have been expected from Weston's calculations[5]. The dextrorotatory isomer, which has an initial rotation of $[\alpha]_D^{21} = 141°$, acquires a rotation of 114° after 5 h; the corresponding specific rotation of the laevorotatory isomer changed from -128° to -97° in 4 h. It was discovered that the decrease in the angle of rotation was due not to racemisation

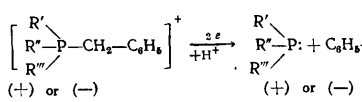
but to oxidation of the phosphine to the phosphine oxide. Molecular asymmetry is entirely probable in the phosphine owing to the presence of a ring containing nitrogen and phosphorus. In the opinion of Campbell and Way, the above azaphosphaphenanthrene proved an unfortunate example for elucidating the possibility of obtaining asymmetric compounds of tervalent phosphorus in an optically active form because of (1) the presence of a ring containing nitrogen and phosphorus, which may itself be a source of molecular asymmetry, and (2) the comparatively ready oxidisability of the phosphine to the phosphine oxide.

In order to avoid these drawbacks, Campbell and Way[7] synthesised a series of substituted phosphafluorenes and their oxides. They were able to resolve 9-phenyl-9-phosphafluorene-2-carboxylic acid



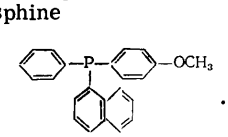
into optical isomers. However, reduction was accompanied by complete racemisation with both optically active oxides: the resulting phosphines were optically inactive. Racemisation of the phosphafluorene was not unexpected, in view of Weston's calculations[5], but it was inconsistent with the result obtained by Campbell and Way for reduction of the azaphosphaphenanthrene oxide[6]. These workers postulate that the participation of the nitrogen atom in the reduction confers on it a stereospecific character in the case of the azaphosphaphenanthrene. Thus Campbell and Way's investigations gave no positive answer to the possible existence of tervalent phosphorus compounds in an optically active form, since molecular asymmetry is possible, besides the asymmetric phosphorus atom, in azaphosphaphenanthrene derivatives, while phosphafluorene derivatives were not obtained in an optically active form.

It was only in 1961 that Horner and his coworkers[8] showed for the first time that asymmetric tertiary phosphines can be resolved into optical antipodes. They reduced the corresponding optically active benzylphosphonium salts at a mercury cathode:



and obtained[8] dextrorotatory methylphenyl-n-propylphosphine $(CH_3)(C_6H_5)(n\text{-}C_3H_7)$ having $[\alpha]_D = +16.8°$ (concentration 5.170 g/100 cm³ toluene), laevorotatory allylmethylphenylphosphine $(CH_2:CH.CH_2)(CH_3)(C_6H_5)P$ having -10.0° (4.5 in toluene), and dextrorotatory ethylmethylphenylphosphine $(C_2H_5)(CH_3)(C_6H_5)P$ having +15 ± 0.5° (6 ± 2 in toluene).

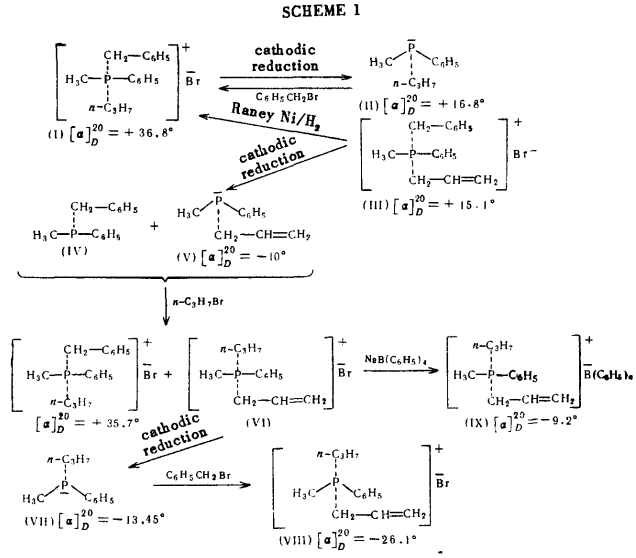
Using the same method, Horner et al.[9] were the first to obtain in an optically active form the asymmetric non-heterocyclic triarylphosphine — *p*-methoxyphenyl-1-naphthylphenylphosphine



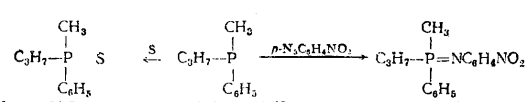
McEwen et al.[10] isolated dextrorotatory and laevorotatory isomers of benzyl-n-butylmethylphosphine having specific rotations $[\alpha]_D^{27}$ of +24 ± 2° and -28.2° (2.9 in benzene), by reducing with sodium methoxide[11] the optically active D(-)- and L(+)-benzyl-n-butyl-2-cyanoethylmethylphosphonium hydrogen dibenzoyltartrates.

Optically active tertiary phosphines proved to be optically far more stable than would have been expected from Weston's calculations[5]. Dextrorotatory methylphenyl-n-propylphosphine was very slowly racemised in boiling toluene[8]. Horner and Winkler[12] found that this compound was racemised according to a first-order equation in high-boiling solvents such as methylnaphthalene, decahydronaphthalene, and n-decane, whereas in diethylaniline and cyclohexanone the kinetics of racemisation was more complicated[12].

SCHEME 1



The separation of racemic asymmetric tertiary phosphines into optical isomers was a remarkable development in the chemistry of phosphorus. The application of optically active tertiary phosphines made possible a very delicate study of the mechanism of the reactions. Horner and his coworkers[8,13], who investigated the interconversion of optically active tertiary phosphines and optically active phosphonium salts (Scheme 1), ascertained that the configuration of the asymmetric phosphorus atom is preserved during these changes. The use of optically active tertiary phosphines facilitated the elucidation of the structure of phosphine dihalides[14-16]. Dextrorotatory and laevoroatory benzyl-n-butylmethylphosphines were converted into the optically active benzyl-n-butylmethylphosphine sulphides by the action of cyclohexene sulphide, monatomic sulphur, and octa-atomic sulphur. The configuration of the asymmetric phosphorus atom was preserved in all these reactions[17]. The reactions of dextrorotatory methylphenyl-n-propylphosphine with sulphur and with *p*-nitrophenyl azide also take place with preservation of the configuration of the asymmetric phosphorus atom[18]:

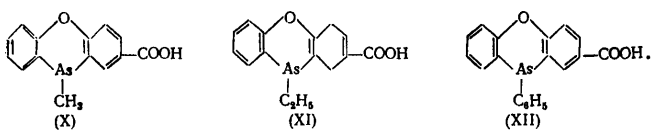


Study of the oxidation of optically active methylphenyl-n-propylphosphine with t-alkyl hydroperoxides[19] confirmed the view expressed previously that the reactions of tertiary

phosphines and phosphites with these hydroperoxides involve nucelophilic attack by hydroxyl oxygen.

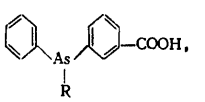
The arsenic atom has the electronic configuration $(1s^2)(2s^2)(2p^6)(3s^2)(3p^6)(3d^{10})(4s^2)(4p^3)$, and, like the phosphorus atom, it may have covalencies of 3–6. Organic derivatives of tervalent arsenic are regarded as derivatives of arsine in which one, two, or three hydrogen atoms have been replaced by organic radicals. Arsines have the configuration of a trigonal pyramid, as is indicated by measurements of dipole moments and by the valency angles determined by different physicochemical methods[20-22]. The oscillation frequency of the arsenic atom in arsine is $16 \times \times 10^4$ s^{-1} [23] (in phosphine it is 5×10^6 s^{-1},[4] and in an amine 2.3×10^{10} s^{-1} [24]). Weston calculated[5] the energy barrier to racemisation of an arsine, the results being expressed as the temperature at which the half-life (or rate of racemisation) would be 2 h. For trimethylarsine this temperature is 107° according to his calculations[5]. Until 1962 no single case had been described of the resolution of an asymmetric tertiary arsine: As(R′R″R‴) into optical isomers.

Tervalent compounds in which arsenic forms part of a cyclic system have been successfully resolved into optical isomers.



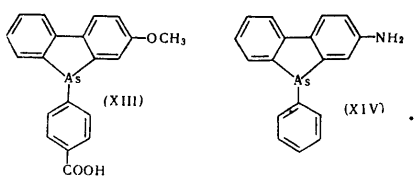
(X) (XI) (XII)

Lesslie and Turner[25] resolved 10-methylphenoxarsine-2-carboxylic acid (X), as well as the 10-ethyl (XI) and 10-phenyl (XII) homologues of this acid. These acids proved to be optically stable, racemising quite slowly even on being heated. Their optical activity is probably due mainly to molecular asymmetry, since the similar acids of tervalent arsenic synthesised by Kamai[26-30], differing from those of Lesslie and Turner in the absence of the oxygen atom linking the two phenyl radicals, and of general formula



could not be resolved into optical antipodes.

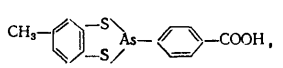
Campbell and Poller[31] resolved the two cyclic compounds of tervalent arsenic — 2-methoxy-9-phenyl-9-arsafluorene-*p*-carboxylic acid (XIII) and 2-amino-9-phenyl-9-arsafluorene (XIV)



(XIII) (XIV)

The isomers thus obtained were optically stable at room temperature.

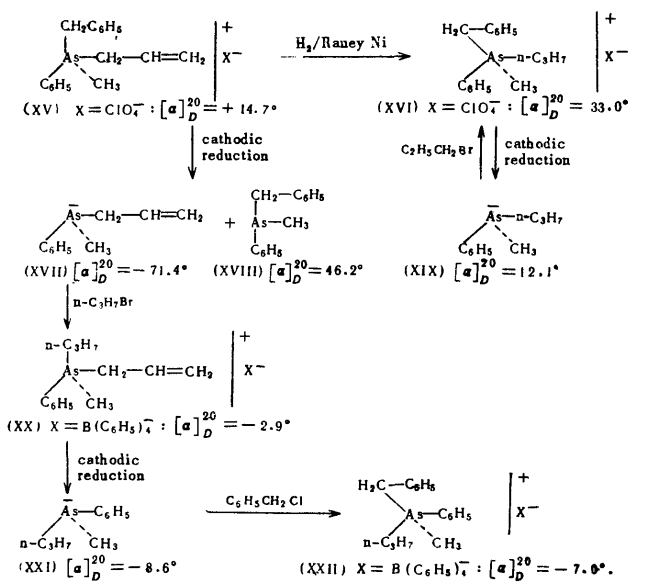
The compound 2-*p*-carboxyphenyl-5-methyl-1,3-dithia-2-arsindane



which was resolved by Campbell[32], was optically stable in chloroform and ethanol, but racemised in aqueous alkali, probably owing to cleavage of an arsenic–sulphur bond. The existence of arsindane enantiomers provides further evidence that arsenic is able to maintain a stable pyramidal configuration when present as a tervalent atom in a heterocyclic compound.

Horner and Fuchs[33] isolated optical isomers of ethylmethylphenylarsine and butylmethylphenylarsine by cathodic reduction of the optically active benzylethylmethylphenylarsonium and benzylbutylmethylphenylarsonium perchlorates by the technique used to reduce quaternary ammonium[34] and phosphonium[35] salts. Dextrorotatory ethylmethylphenylarsine $(C_2H_5)(CH_3)(C_6H_5)As$ boiled at 64–65° (3.3 mm) and had a specific rotation $[\alpha]_D^{20}$ of 1.9°, while the laevorotatory isomer of this arsine boiled at 69–71° (4 mm) and had a specific rotation of -1.15°. The corresponding optically active arsine sulphides were isolated by the addition of sulphur to the optically active arsines.

SCHEME 2



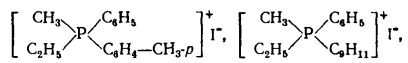
Horner and Fuchs[36] studied the interconversion of optically active tertiary arsines and quaternary arsonium salts (Scheme 2). The interconversions (XVI) → (XVII) and (XVII) → (XVI) indicate that the configuration of the arsenic atom is maintained during these changes. Compounds (XVIII) and (XIX) were separated by distillation. The difference in rotation between (XXI) and (XVII) (with the opposite sign of rotation) is explained by partial racemisation of (XX), since optically active quaternary arsonium halides (in contrast to the sulphates and perchlorates) are more or less rapidly racemised in organic solvents. The arsonium salts (XV) and (XVI) have the same configuration, since the asymmetric centre is unaffected by catalytic hydrogenation.

The preparation of stable optically active non-heterocyclic tertiary phosphines and arsines has been an important event in the stereochemistry of organophosphorus and organoarsenic compounds: it has opened up a path for the stereochemical study of reaction mechanisms involving asymmetric phosphorus and arsenic atoms, and it has

shown once again that certain concepts which have been regarded as "absolute" at some stage in the development of science prove to be "extremely relative" and yield place to new concepts, which are sometimes the direct opposite. This has occurred in connection with the oscillation of tervalent phosphorus and arsenic atoms in phosphines and arsines. Until recently the vast majority of investigators regarded the presence of this oscillation as indisputable. The researches of Horner and his collaborators [8-10,12,13,17,18,33,36] have now convincingly demonstrated that tervalent phosphorus and arsenic atoms do not undergo such oscillation.

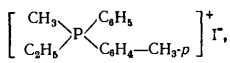
III. STEREOCHEMISTRY OF QUATERNARY PHOSPHONIUM AND ARSONIUM COMPOUNDS

The first attempts to resolve unsymmetrical phosphonium and arsonium compounds into optical antipodes were made at the beginning of the present century. Michaelis [37,38] synthesised and tried to resolve ethylmethylphenyl-*p*-tolylphosphonium iodide (I), ethylmethylphenyl-2,4,5-trimethylphenylphosphonium iodide (II)



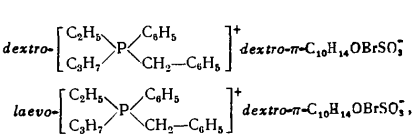
(I) (II)

and ethylmethylphenyl-*p*-tolylarsonium iodide (III)



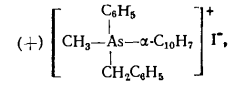
(III)

but no positive results were obtained. Wedekind [39] tried unsuccessfully to resolve ethylmethylphenyl-*p*-tolylphosphonium and benzylmethylphenyl-*p*-tolylphosphonium iodides. Winmill [40] was likewise unsuccessful in resolving a series of unsymmetrical arsonium salts into optical isomers. Nor did the endeavours of Radcliffe and Brindley [41], Meisenheimer [2], or Kamai [42] lead to a positive result. Meisenheimer considered that all the failures in resolving asymmetric phosphonium salts of the type [abcdP]Hal into optical antipodes were due merely to experimental difficulties, since the salts [Pabc(OH)]X (oxides with *dextro*-π-bromocamphorsulphonic acid) were obtained in an optically active form [1,2]. Kamai and Khismatullina [43] were able to isolate the crystalline *dextro*-π-bromocamphorsulphonate salt from allylbenzylbutylphenylphosphonium bromide. Two diastereoisomeric *dextro*-π-bromocamphorsulphonates

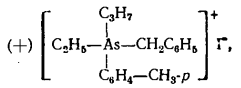


were obtained from allylbenzylethylphenylphosphonium bromide, but the individual isomers could not be isolated when these diastereoisomers were decomposed, this being explained by the great experimental difficulties. Kumli et al. [44] successfully resolved a non-heterocyclic phosphonium salt — benzylethylmethylphenylphosphonium iodide — into optical antipodes, as will be discussed in greater detail later.

Experiments on the resolution of asymmetric arsonium salts have proved more successful. Burrows and Turner [3] isolated the dextrorotatory isomer of benzylmethyl-1-naphthylphenylarsonium iodide



having a maximum rotation of $[\alpha]_D = 0.1°$ and $[M]_D = 12°$ in alcoholic acetone; the rotation of the solution fell rapidly even at room temperature. Kamai [45] isolated the dextrorotatory isomer of benzylethylpropyl-*p*-tolylarsonium iodide



with a rotation of $[\alpha]_D = 9.86°$ and $[M]_D = 45°$. The salt lost its optical activity very rapidly. Kamai and Gatilov [46] resolved benzylethylpentylphenylarsonium bromide, but the optical isomers rapidly racemised when isolated. These workers [47] separated dextrorotatory and laevorotatory isomers of benzylethylpentylphenylarsonium iodide by adsorption on dextrorotatory and laevorotatory quartz, but the isomers rapidly lost their optical activity. Thus the optical isomers of arsonium halides are optically unstable and racemise rapidly, whereas, as recent investigations by Horner [36] have shown, arsonium perchlorates are optically stable.

Quaternary ammonium halides often racemise comparatively rapidly in such solvents as chloroform, whereas the sulphates and nitrates possess greater stability. Pope and Harvey [48] suggested that this racemisation is due to equilibrium dissociation of quaternary ammonium halides into a tertiary amine and an alkyl or aryl halide:

$$[abcdN]\,Hal \rightleftarrows abcN + dHal,$$

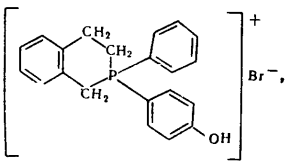
which in their view explained the optical stability of the nitrates and sulphates, these being incapable of undergoing such ready dissociation as the quaternary ammonium halides. Burrows and Turner [3] assumed that the instability of optically active non-heterocyclic arsonium salts was due to the occurrence of similar equilibrium dissociation in solution, and obtained some evidence for this assumption. They showed [3] that, if dimethylphenylarsine is treated with ethyl iodide, ethyldimethylphenylarsonium iodide is formed mixed with a considerable quantity of phenyltrimethylarsonium iodide:

$$(CH_3)_2(C_6H_5)As + C_2H_5I \rightleftarrows [(CH_3)_2(C_2H_5)(C_6H_5)As]I \rightleftarrows CH_3I + (CH_3)(C_2H_5)(C_6H_5)As,$$
$$(CH_3)_2(C_6H_5)As + CH_3I \rightleftarrows [(CH_3)_3(C_6H_5)As]I.$$

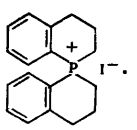
These results are readily explained by the equilibrium dissociation theory.

Mann [49] tried to explain by the presence of equilibrium dissociation the numerous unsuccessful attempts to resolve asymmetric phosphonium salts of the type [abcdP]Hal into optical antipodes, although Wedekind [39] had shown long before that ethylmethylphenyl-*p*-tolylphosphonium iodide does not dissociate into an alkyl or aryl halide and a tertiary phosphine in chloroform solution at room temperature or at the boiling point of chloroform. Holliman and Mann [49] attempted to resolve into optical antipodes two phosphonium salts — 1,2,3,4-tetrahydro-2-*p*-hydroxyphenyl-2-phenyl-phosphinolinium and -isophosphinolinium

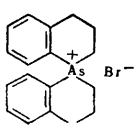
bromides — which were structurally incapable of dissociating into a tertiary phosphine and an alkyl halide. All attempts at the resolution of the former compound were unsuccessful, but a dextrorotatory form of the isophosphinolinium bromide



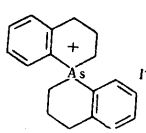
was isolated having a molecular rotation of $[M]_D = 32.9°$, although attempts to repeat its separation were unsuccessful. Hart and Mann[50] synthesised and successfully resolved into optical isomers a spirocyclic phosphonium salt possessing molecular asymmetry — *P*-spirobi-1,2,3,4-tetrahydrophosphinolinium iodide



The resolution of this salt was proof of the tetrahedral configuration of the phosphonium cation. Holliman and Mann's work[51,52] on the resolution of two spirocyclic arsonium salts — *As*-spirobi-1,2,3,4-tetrahydroarsinolinium bromide

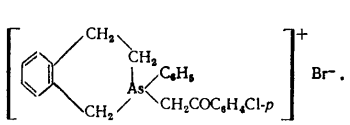


and the isomeric iodide



— confirmed the tetrahedral configuration of the tetrasubstituted arsonium cation. The isomers of the spirocyclic arsonium salts were optically stable.

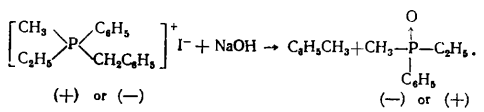
Holliman and Mann[53] resolved 1,2,3,4-tetrahydro-2-*p*-chlorophenacyl-2-phenylisoarsinolinium bromide



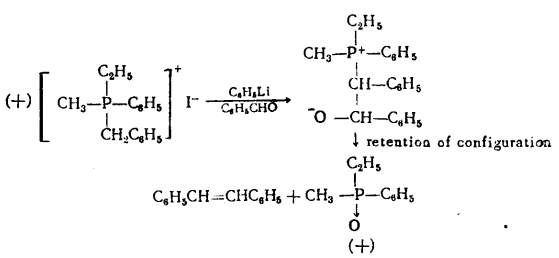
The isomers possessed relatively high optical stability, the rotation changing, in chloroform solution at room temperature, over the course of 5 days. The optical stability is assumed to be a consequence of the great chemical stability of this compound.

As already noted above, the first successful resolution of a non-heterocyclic asymmetric phosphonium salt — benzylethylmethylphenylphosphonium iodide — was accomplished by Kumli et al.[44] by means of the silver hydrogen salts of dextrorotatory and laevorotatory dibenzoyltartaric acid. The benzylethylmethylphenylphosphonium iodide isomers thus obtained were optically stable. The dextrorotatory benzylethylmethyl-*p*-tolyphosphonium chloride, bromide, and iodide prepared by Kamai and Usacheva[54] also exhibited high optical stability, which supports Wedekind's conclusion that equilibrium dissociation into a tertiary phosphine and an alkyl or aryl halide is absent in non-heterocyclic quaternary phosphonium salts containing at least one alkyl group attached to the phosphorus atom.

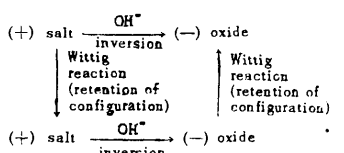
Kumli and his coworkers studied the conversion of dextrorotatory and laevorotatory benzylethylmethylphenylphosphonium iodide into the corresponding optically active ethylmethylphenylphosphine oxides:



This is a third-order reaction — of first order with respect to the concentration of phosphonium salt and of second order with respect to the concentration of sodium hydroxide[55] — involving inversion of the configuration of the asymmetric phosphorus atom[56]. The dextrorotatory benzylethylmethylphenylphosphonium iodide gave with inversion 100% of the laevorotatory ethylmethylphenylphosphine oxide, and the laevorotatory isomer of the phosphonium salt yielded dextrorotatory ethylmethylphenylphosphine oxide. In the Witting reaction with the optical isomers of benzylethylmethylphenylphosphonium iodide, the configuration of the phosphorus atom was maintained[56,57]:



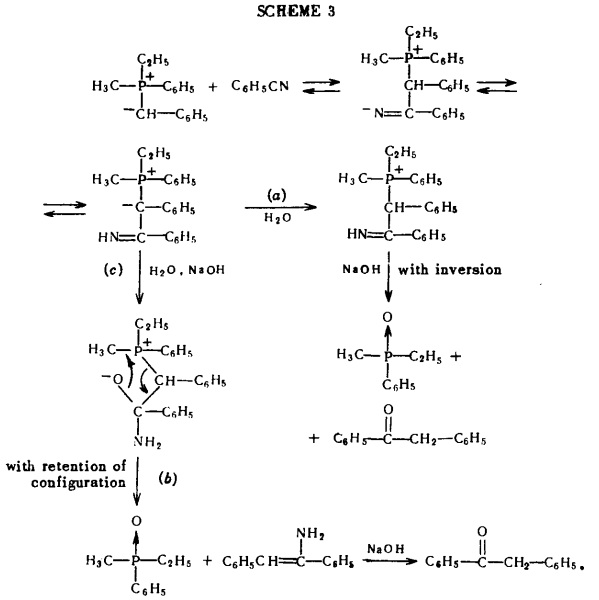
The two conversions of the optically active phosphonium isomers can be represented in the form of a cycle of processes:



Bladé-Font et al. studied the stereochemical course of the reaction of optically active ethylmethylphenylbenzylidenephosphorane[58], prepared by the interaction of laevorotatory

benzylethylmethylphenylphosphonium iodide with phenyl-lithium[44,56], with benzonitrile (see Scheme 3).

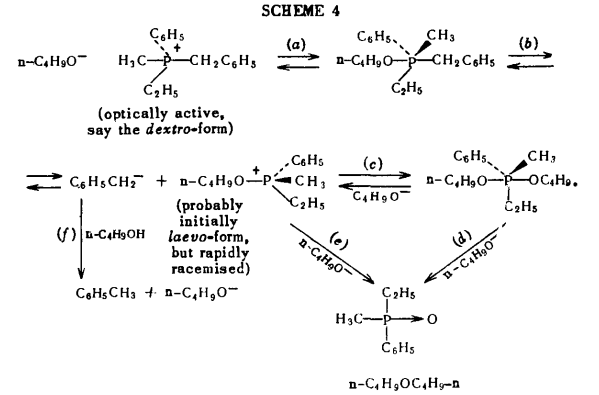
SCHEME 3



It was calculated that the reaction was accompanied by 68% inversion of configuration at the asymmetric phosphorus atom. They supposed that two competing reactions were taking place, one of which (*a*) gave ethylmethylphenylphosphine oxide with inversion of configuration, while the other reaction (*b*) gave the same oxide with maintenance of the configuration. Quite recently the reaction of optically active ethylmethylphenylbenzylidenephosphorane with styrene oxide has been studied[59], and shown to give ethylmethylphenylphosphine oxide with 50% inversion of configuration at the asymmetric phosphorus atom.

Grayson and Keough[60] showed that phosphonium alkoxides of the type $[R_3PCH_2C_6H_5]^+OR^-$ yield on decomposition toluene, a phosphine oxide, and an ether. Parisek et al.[61] investigated the stereochemistry of this reaction with optical isomers of benzylethylmethylphenylphosphonium n-butoxide, obtained from sodium n-butoxide and the optical isomers of the phosphonium iodide. Decomposition of the optically active phosphonium n-butoxide yielded ethylmethylphenylphosphine oxide with almost complete racemisation. This result can be explained by a reaction mechanism in which stage (*d*) or (*e*) is the slowest, whereas stage (*f*) is comparatively rapid (Scheme 4).

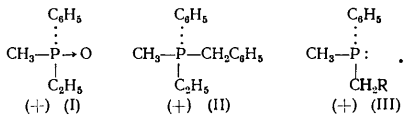
SCHEME 4



IV. STEREOCHEMISTRY OF OXIDES AND SULPHIDES OF PHOSPHORUS AND ARSENIC

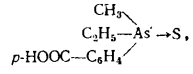
Meisenheimer and Lichtenstadt[1] were the first to show that phosphorus can give optically active compounds. Successful experimental resolutions of the oxides of tertiary amines into optical enantiomers[62,63] led Meisenheimer to study asymmetric phosphine oxides. By means of *dextro*-π-bromocamphorsulphonic acid he was able to isolate a dextrorotatory isomer of ethylmethylphenylphosphine oxide having a molecular rotation of $[M]_D = 50°$ and high optical stability. It is interesting that the value calculated by Sokolov and Reutov[64] for the molecular rotation of this phosphine oxide, using Brewster's rule of conformational asymmetry[65], is close to the value found experimentally[2] and by Meisenheimer[1,2]: a calculated value[64] of 40° compares with experimental values[2] of 47° in benzene and 40° in water or hydrochloric acid.

The laevorotatory isomer of ethylmethylphenylphosphine oxide was obtained by Meisenheimer only 14 years later[2]. The isolation of optically active isomers of this oxide, and later of benzylmethylphenylphosphine oxide[2], permitted Meisenheimer to conclude that phosphorus, like nitrogen, is able to give optically active compounds, for which it is sufficient to replace the five valencies of phosphorus by four different radicals. At the present time new paths for the synthesis of optically active oxides of tertiary phosphines have been opened as a result of the excellent work done by Horner et al.[8] and by Kumli and his coworkers[44,55,56] — (1) by the oxidation of optically active tertiary phosphines[8] and (2) by the action of sodium hydroxide on optically active phosphonium salts or by the Wittig reaction on the latter[55,56].



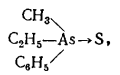
Sokolov and Reutov[64] assign the absolute configuration (I) to the dextrorotatory ethylmethylphenylphosphine oxide, on the basis of theoretical calculations of the molecular rotation of this isomer from Brewster's molecular asymmetry rule[65] and the indication by Limburg[66] that this rule correctly predicts the sign of rotation of compounds containing an asymmetric silicon atom. Since the configurational relationship among (I)–(III) has been established[67], (II) represents the absolute configuration of the optically active tetrasubstituted phosphonium cation, while (III) is the absolute configuration of the optically active tertiary phosphine.

Oxides of tertiary arsines have not yet been prepared in optically active form. The reason for this is still not understood. Sulphides of arsenic, on the other hand, have been successfully resolved into optical isomers. Mills and Raper[68] prepared optical isomers of *p*-carboxyphenylethylmethylarsine sulphide



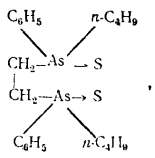
having rotations $[M]_{5780}$ of 51° and -52°. Both isomers possessed considerable optical stability: an aqueous solution of the sodium salt remained optically unchanged on

prolonged boiling. Horner and Fuchs[33] obtained dextrorotatory ethylmethylphenylarsine sulphide



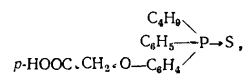
with a rotation of $[\alpha]_D^{20} = 24.5°$, by the addition of sulphur to the dextrorotatory arsine.

Chatt and Mann[69] isolated two forms of ethylene-1,2--bis-(n-butylphenylarsine sulphide)



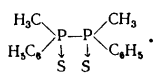
but were unable to determine which was racemic and which was the *meso*-form.

Davies and Mann[70] were the first to resolve butyl-*p*--carboxymethoxyphenylphenylphosphine sulphide

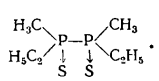


the resulting isomers having rotations $[M]_D$ of 9.6° and -9.7° with relatively high optical stability. The work of Horner[8] has opened up a new path for the synthesis of optically active phosphine sulphides, by the addition of sulphur to optically active tertiary phosphines.

Wheatley[71] isolated two forms (*meso* and racemic) of 1,2-dimethyl-1,2-diphenyldiphosphine disulphide

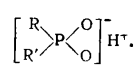


He established by means of X-rays that the modification having the higher melting point was centrosymmetric and represented the *meso*-form, while the other modification was the racemic form. Maier[72] tried to resolve the racemate by chromatographic adsorption on D(-)-mannitol, D(-)-lactose, and calcium D(-)-tartrate, but was unsuccessful. He isolated[72] two forms (racemic and *meso*) of 1,2-diethyl-1,2-dimethyldiphosphine disulphide

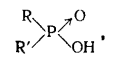


V. STEREOCHEMISTRY OF ORGANIC ACIDS OF PHOSPHORUS AND ARSENIC AND OF THEIR DERIVATIVES

Interest in the organic acids of four-coordinate phosphorus from the point of view of stereochemical research arose as long ago as the beginning of the twentieth century. Kipping and Luff[73,74] were the first to try to resolve the phenyl *p*-tolyl and phenyl 2-naphthyl esters of phosphoric acid, but without success. Nor was a positive result obtained from Pope and Gibson's experiments[75] on the separation of methylphenylphosphinic acid into optical isomers or from those of Turner[76] on the resolution of benzylphenylarsinic acid. The former workers[75] tried to explain their failure by the ease of transformation of the phosphinic acid into the ortho-form $(CH_3)(C_6H_5)P(OH)_3$, which entails loss of asymmetry at the phosphorus atom. The optical inactivity of compounds containing hydroxyl and double-bonded oxygen attached to the phosphorus atom can be explained on the basis of Werner's theory, as Meisenheimer[77] did mainly for ammonium, phosphonium, and similar compounds. The structure of phosphorus compounds of the type RR'P(O)OH can be represented

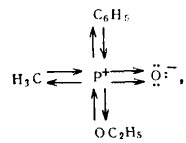


In this case the inner complex is not asymmetric. The replaceable hydrogen in the outer sphere does not affect the asymmetry of the molecule. It was deduced on the basis of these arguments that compounds of the type



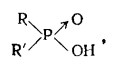
cannot be obtained in an optically active form.

Gibson and Johnson[78], starting from the electronic theory, reached the opposite conclusion. In their opinion the structure of ethyl methylphenylphosphinate can be written



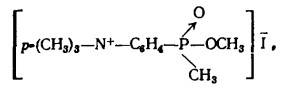
in which it can be seen that the outer octet of the phosphorus atom is complete without the oxygen atom. The octet of the oxygen atom can be complete only if the lone pair of electrons of the phosphorus atom are distributed between the two atoms, as is represented by the two arrows pointing in the same direction. The phosphorus atom thus becomes positive, while the oxygen becomes negative. The phosphorus–oxygen bond most probably becomes semipolar, as is confirmed by the change in parachor[79].

It would appear that compounds of the type

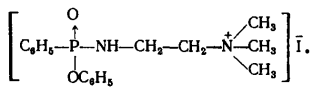


should exist in an optically active form. However, experiments by A. E. and B. A. Arbuzov[80] on the resolution of asymmetric phosphonecarboxylic acids, as well as those of A. E. Arbuzov and I. A. Arbuzova[81] on the resolution of isobutylphenylphosphinic and phenyltriphenylmethylphosphinic acids, did not yield a positive result. It was only in 1956 that Coyne[82], Marsi[83], and their collaborators obtained optically active forms of asymmetric derivatives

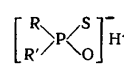
of phosphinic acids, as the quaternary ammonium salts — *p*-methoxy(methyl)phosphinylphenyltrimethylammonium iodide



and trimethyl-2-phenoxy(phenyl)phosphinylaminoethylammonium iodide

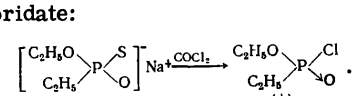


The first attempts to resolve asymmetric phosphinothioic acids, whose structure remains asymmetric



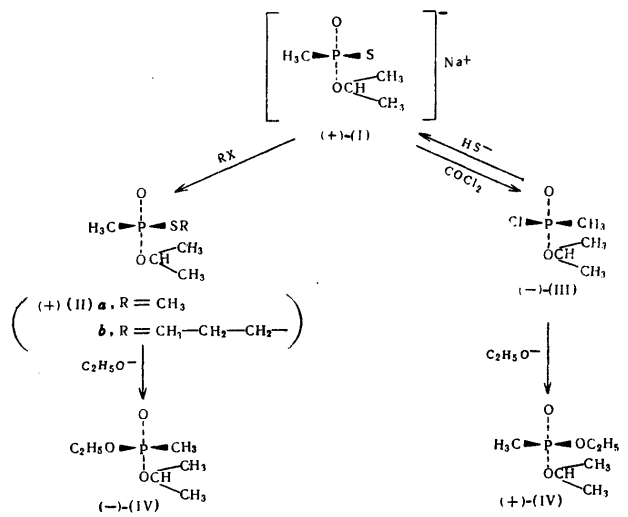
on Werner's coordination theory, were unsuccessful. Arbuzov and Kamai[84] prepared a series of these acids RR'PSOH, and hoped to separate them into optical isomers, since Mills and Raper[68] had successfully resolved the arsine sulphides RR'R"As → S, which were closely similar in type. Their experiments yielded no positive result. Aaron and Miller[85] were the first to resolve a derivative of phosphonothioic acid — ethyl hydrogen ethylphosphonothioate $C_2H_5PS(OC_2H_5)OH$ — by means of quinone. The isomers were isolated in the form of the dicyclohexylammonium salts, and were optically stable[86]. Subsequently[87] five more *O*-alkyl hydrogen alkylphosphonothioates — the ethyl, isopropyl, and methyl *P*-methyl esters, the ethyl *P*-isopropyl ester, and the methyl *P*-ethyl ester — were resolved via the brucine and quinine salts. The synthesis of racemic *O*-alkyl hydrogen alkylphosphonothioates has been described by Kabachnik et al.[88] and by Hoffmann et al.[89] Green and Hudson[90] resolved ethyl(phenyl)phosphinothiolic acid $C_2H_5(C_6H_5)POSH$, and Michalski et al.[91] have resolved *OO'*-dialkyl hydrogen phosphorothioates — the butyl ethyl and the ethyl isopropyl esters — through the cinchonine and cinchonidine salts. The successful separation of asymmetric derivatives of phosphinothioic acids has opened a new chapter in the investigation of optically active organophosphorus compounds, by permitting the study of (1) the stereochemistry of substitution reactions at an asymmetric phosphorus atom and (2) the biological activity of optical isomers of organophosphorus compounds.

By treating racemic *O*-ethyl hydrogen ethylphosphonothioate and its laevorotatory isomer with carbonyl chloride, Aaron[92] was able to isolate racemic ethyl ethylphosphonochloridate. By the action of carbonyl chloride on the sodium salt of laevorotatory *O*-ethyl hydrogen ethylphosphonothioate be obtained dextrorotatory *O*-ethyl ethylphosphonochloridate:



The racemisation half-life of the isolated optically active acid chloride was 6 h in dry acetone and 4 days in dry benzene at room temperature. The action of carbonyl chloride on dextrorotatory sodium *O*-isopropyl methylphosphonothioate gave laevorotatory *O*-isopropyl methylphosphonochloridate[92], irrespectively of whether the reaction took place in hexane, acetone, or dioxan.

SCHEME 5

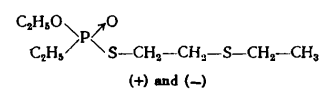


The optically active acid chloride thus obtained was subjected to various reactions as indicated in Scheme 5, the relative configurations of the compounds in which were deduced by the following reasoning. Dextrorotatory *O*-isopropyl *S*-methyl methylphosphonothiolate (+)-(II*a*) and laevorotatory *O*-isopropyl methylphosphonochloridate (-)-(III) were converted by the action of the ethoxide ion into the optical antipodes of ethyl isopropyl methylphosphonate:

(+)-(II*a*) → (−)-(IV) and (−)-(III) → (+)-(IV).

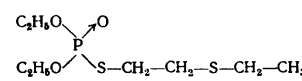
The compounds (+)-(II*a*) and (-)-(III) probably had opposite configurations. The compounds (+)-(II*a*) and (+)-(II*b*) had the same sign of rotation and the same configuration. This was confirmed by the synthesis of both laevorotatory esters from laevorotatory sodium *O*-isopropyl methylphosphonothioate (I) under conditions such that the *S*-alkylated product was formed exclusively[93].

Aaron and Michel[94] used the optical isomers of *OO'*-diethyl hydrogen phosphorothioate to synthesise dextrorotatory and laevorotatory ethyl *S*-2-ethylthioethyl ethylphosphonothiolate



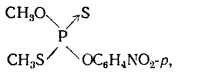
(+) and (−)

which were similar to the cholinesterase-inhibitor diethyl *S*-2-ethylthioethyl phosphorothiolate[95]

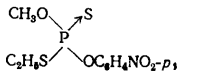


Study of the rate of suppression of cholinesterase by the two optical isomers of ethyl *S*-2-ethylthioethyl ethylphosphonothiolate showed that the laevorotatory isomer was a stronger inhibitor than the dextrorotatory isomer by a factor of 10–20.

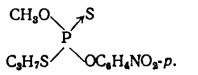
The difference in physiological activity between isomeric thionates and thiolates of phosphorus[95,96] and the biological activity of *cis* and *trans*-isomers of vinyl[97] and propenyl phosphates[98] led Hilgetag and Lehmann[99] to prepare the optically active thiophosphates — *OS*-dimethyl *O'*-*p*-nitrophenyl phosphorothiolothionate



S-ethyl *O*-methyl *O'*-*p*-nitrophenyl phosphorothiolothionate

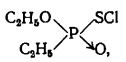


and *O*-methyl *O'*-*p*-nitrophenyl *S*-propyl phosphorothiolothionate



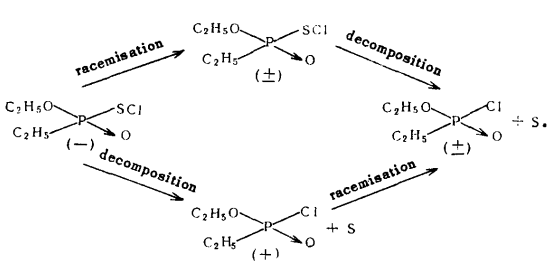
The optical isomers of *OS*-dimethyl *O'*-*p*-nitrophenyl phosphorothiolothionate were tested biologically on the fly *Drosophila funebris*. The enantiomers had the same effect on the fly, but exhibited different toxicities towards warm-blooded creatures: the values of LD_{50} were 135 and 25 mg kg^{-1} (mouse) for the dextrorotatory and laevorotatory isomers respectively.

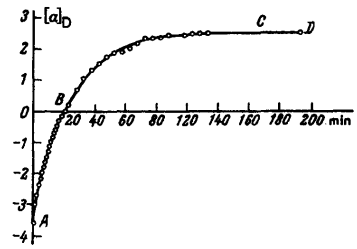
Very interesting investigations have recently been made by Michalski and Ratajczak with the optical isomers of *O*-ethyl hydrogen ethylphosphonothioate, which had been obtained by Aaron et al.[85] These were converted by means of sulphuryl chloride into the optically active sulphenyl chlorides[100,101]



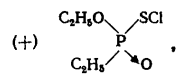
which lost their optical activity comparatively rapidly (racemisation half-life 6.8 min)[101]. A detailed study was made of the behaviour of laevorotatory ethyl chlorothio-(ethyl)phosphinate[101]. The rotation of this isomer changed from (-) to (+) only a few minutes after preparation, reached a maximum value in 3 h, and then gradually fell to zero. This variation in rotation of the laevorotatory sulphenyl chloride was explained[101] not only by racemisation but also by chemical changes, the sulphenyl chloride gradually decomposing into ethyl ethylphosphonochloridate and sulphur, with the former product also racemising comparatively rapidly.

The changes undergone by the laevorotatory ethyl chlorothio(ethyl)phosphinate were represented[101] by the cyclic scheme (see also diagram)

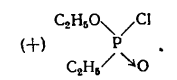




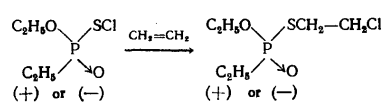
The diagram shows that the section *AB* of the curve predominates in racemisation of the dextrorotatory sulphenyl chloride itself



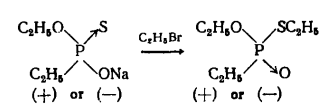
and corresponds to a first-order reaction. Section *CD* represents racemisation of dextrorotatory ethyl ethylphosphonochloridate



Addition of ethylene to the optically active ethyl chlorothio(ethyl)phosphinates gave dextrorotatory and laevorotatory *S*-alkyl esters[101,102]:



These were written A–S–R, where A = $C_2H_5OPO(C_2H_5)$– and R = $ClCH_2CH_2$–. Dextrorotatory and laevorotatory sodium *O*-ethyl ethylphosphonothioate gave with ethyl bromide the dextrorotatory and laevorotatory ethylthio-derivatives:



or A–S–C_2H_5. Michalski and Ratajczak[102] first studied the conversion of both dextrorotatory *S*-alkyl esters A–S–R

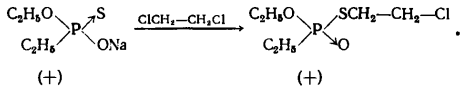
$$\begin{cases} A = (C_2H_5O)(C_2H_5)P(O)— \\ R = ClCH_2—CH_2—,\ C_2H_5 \end{cases}$$

into the optically active ethyl ethylphosphonochloridates by chlorolysis of the P–S bond:

$$A—S—R \longrightarrow A—Cl + R—S—Cl \quad \begin{cases} A = (C_2H_5O)(C_2H_5)P(O)— \\ R = ClCH_2—CH_2—,\ CH_3—CH_2— \end{cases}$$

Michalski and Ratajczak then carried out a similar reaction with the laevorotatory alkyl *S*-alkyl esters A–S–R.[103] They discovered that the direction of chlorolysis of the optically active alkyl alkylthio-derivatives A–S–R (where R = $ClCH_2CH_2$ and C_2H_5) to the acid chlorides A–Cl was

affected by the nature of the aliphatic radical attached to the sulphur: chlorolysis of the dextrorotatory *S*-alkyl ester (+)-$C_2H_5OPO(C_2H_5)SCH_2CH_2Cl$ gave the dextrorotatory ethyl ethylphosphonochloridate (+)-$C_2H_5OPO(C_2H_5)Cl$, whereas chlorolysis of the dextrorotatory *S*-alkyl ester (+)-$C_2H_5OPO(C_2H_5)SCH_2CH_3$ yielded the laevorotatory ethyl ethylphosphonochloridate (-)-$C_2H_5OPO(C_2H_5)Cl$. The two initial dextrorotatory *S*-alkyl esters A–S–R have the same configuration, since the dextrorotatory chloroethylthio-derivative was obtained also by reaction of dextrorotatory potassium or sodium *O*-ethyl ethylphosphonothioate with dichloroethane:



This reaction probably occurs without inversion of configuration at the asymmetric phosphorus atom, since the bonds around it are not involved.

Thus the dextrorotatory *S*-alkyl esters

$$(+)\,(C_2H_5O)\,(C_2H_5)\,P\,(O)\,SCH_2-CH_2-Cl \text{ and } (+)\,(C_2H_5O)\,(C_2H_5)\,P\,(O)\,S-CH_2-CH_3,$$

have the same configuration, whereas the ethyl ethylphosphonochloridates obtained from them by chlorolysis of the P–S bond have opposite configurations. Most probably chlorolysis of the two *S*-alkyl esters takes place by different mechanisms, the configuration being preserved with the chloroethylthio-derivative and inverted with the ethylthio-derivative. This mechanism for the latter derivative is supported also by the fact that laevorotatory ethyl ethylphosphonochloridate is converted into dextrorotatory diethyl ethylphosphonothiolate on treatment with sodium ethyl sulphide:

$$(-)\,(C_2H_5O)\,(C_2H_5)\,P\,(O)\,Cl \xrightarrow{C_2H_5SNa} (+)\,(C_2H_5O)\,(C_2H_5)\,P\,(O)\,S-CH_2-CH_3,$$

the reaction involving inversion of configuration at the asymmetric phosphorus atom [104].

In order to investigate the effect of chlorine in the side-chain on the stereochemical course of chlorolysis of *S*-alkyl esters A–S–R, the optically active compounds

$$(C_2H_5O)\,(C_2H_5)\,P\,(O)\,SCH_2-CH_2-CH_2-Cl,$$
$$(C_2H_5O)\,(C_2H_5)\,P\,(O)\,SCH_2-CH_2-CH_2-CH_2-Cl,$$

were examined. Chlorolysis of both these alkylthio--derivatives is accompanied by inversion of configuration at the asymmetric phosphorus atom. Table 1 lists results obtained for the chlorolysis to optically active ethyl ethylphosphonochloridates of all the optically active *S*-alkyl esters $C_2H_5OPO(C_2H_5)SR$ studied [103].

Ratajczak [105] studied the substitution of optically active ethyl ethylphosphonochloridates with various nucelophilic reagents such as RS^-, RO^-, R_2NH, and $C_2H_5OPS(C_2H_5)O^-$. Since kinetic data [104,106] indicate that the reactions of various organophosphorus acid chlorides with nucleophilic reagents have an S_N2 mechanism, while Ratajczak [107] and Green and Hudson [108,109] have shown that substitutions at the phosphorus atom under similar conditions involve inversion, Ratajczak [105] postulated that the reactions of optically active ethyl ethylphosphonochloridates with the

TABLE 1.

$(C_2H_5O)\,(C_2H_5)P(O)SR \rightarrow (C_2H_5O)\,(C_2H_5)P(O)Cl$

Rotation of S-alkyl ester	R	Rotation of acid chloride	Steric effect
(−)	C_2H_5	(+)	inversion
(+)	C_2H_5	(−)	inversion
(−)	CH_2-CH_2-Cl	(−)	retention
(+)	CH_2-CH_2-Cl	(+)	retention
(+)	$CH_2-CH_2-CH_2-Cl$	(−)	inversion
(−)	$CH_2-CH_2-CH_2-CH_2-Cl$	(+)	inversion

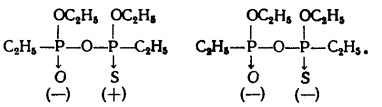
TABLE 2.

$(C_2H_5O)\,(C_2H_5)\,P\,(O)\,Cl\,(II) + :B \rightarrow (C_2H_5O)\,(C_2H_5)\,P\,(O)\,B + Cl^-$

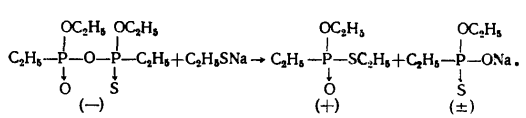
No. of reaction	$[\alpha]_D$, deg (II)	Nucleophile B	Substitution product	$[\alpha]_D$, deg product
(1)	−15	$C_2H_5S^-$	$(C_2H_5O)(C_2H_5)P(O)SC_2H_5$ (III)	+10.30
(2)	−13	$C_4H_9S^-$	$(C_2H_5O)(C_2H_5)P(O)SC_4H_9$ (IV)	+8.28
(3)	+15	$(C_4H_9)_2NH$	$(C_2H_5O)(C_2H_5)P(O)N(C_4H_9)_2$ (V)	−4.30
(4)	−37.10	CH_3O^-	$(C_2H_5O)(C_2H_5)P(O)OCH_3$ (VI)	−0.80
	−12.40	CH_3O^-	$(C_2H_5O)(C_2H_5)P(O)OCH_3$ (VI)	+0.40
(5)	40.05	$(\pm)(C_2H_5O)\,(C_2H_5)P(S)O^-$	$(C_2H_5O)(C_2H_5)P(O)-O-P(S)(OC_2H_5)C_2H_5$ (VII)	−10.90
	−10.50	$(\pm)(C_2H_5O)\,(C_2H_5)P(S)O^-$	$(C_2H_5O)(C_2H_5)P(O)-O-P(S)(OC_2H_5)C_2H_5$ (VII)	+1.85

above nucleophilic reagents entail inversion of configuration at the asymmetric phosphorus atom. The results obtained are indicated in Table 2.[105]

Of the compounds listed in Table 2, special interest attaches to (VII), obtained by reaction (5)[107]. It contains two asymmetric centres PO and PS, and can exist in four optically active and two racemic forms. Since thio-acids are acylated at the oxygen atom[101], the pyrophosphonothionate (VII) should exist as a mixture of diastereoisomers

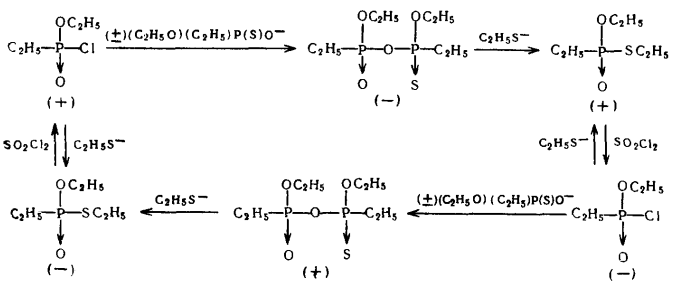


Studies had previously been made of the reactions of pyrophosphonothionates with the nucleophilic reagents sodium methoxide [110,111] and dimethylamine [112]. The latter were shown to attack the more electrophilic phosphorus (P→O) in the pyrophosphonothionate. Since organophosphorus anhydrides react with nucleophilic reagents by an S_N2 mechanism [113], it was supposed that reactions of the latter with pyrophosphonothionates should entail inversion [112]. The pyrophosphonothionate (-)-(VII) (Table 2) reacted with sodium ethyl sulphide to form racemic sodium *O*-ethyl ethylphosphonothioate and dextrorotatory diethyl ethylphosphonothiolate [107]:

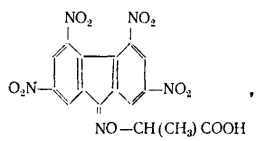


All the transformations of optically active acids of quadricovalent phosphorus derivatives studied Michalski and Ratajczak [103,105,107] can be summarised in the form of a

cycle similar to the Walden cycle in the chemistry of carbon, in which every change involves inversion[107]:

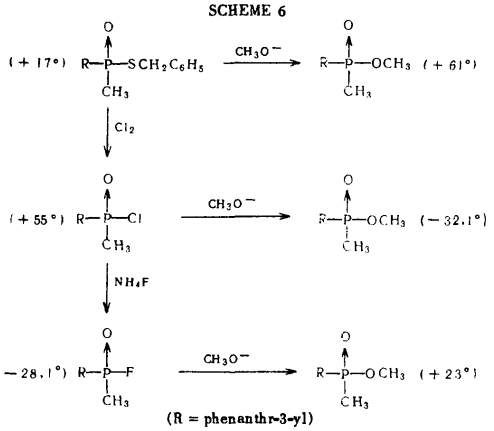


A very interesting method which has recently been discovered for resolving racemates into optical isomers is based on the spontaneous selective crystallisation of inclusion compounds formed by a complexing agent of open spiral structure with molecules of the compound to be separated which have penetrated into the cavities in its lattice[114]. Green and Hudson[115] isolated, via inclusion products with α-(2,4,5,7-tetranitrofluoren-9-ylideneamino-oxy)propionic acid



the dextrorotatory isomer of methyl 1-naphthyl methylphosphonate (+)-(1-$C_{10}H_7O$)CH_3POOCH_3 and both optical isomers of benzyl methyl(phenanthr-3-yl)phosphinothiolate. They used the dextrorotatory isomer of the ester to study[116] some of the substitutions shown in Scheme 6.

SCHEME 6



(R = phenanthr-3-yl)

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Research on the stereochemistry of organic compounds of phosphorus and arsenic, begun as long ago as the beginning of the century, entered a new phase around 1956–1959. Whereas before 1956 workers had devoted their efforts mainly to preparing individual representatives of various classes of organophosphorus and organoarsenic compounds in an optically active form, during recent years serious investigations have been started on the mechanism of various reactions involving optically active compounds of phosphorus and arsenic, and some interesting results have already been obtained. There is no doubt that the amount of work done on the stereochemistry of organic compounds of phosphorus and arsenic will increase every year, and will lead to still more interesting results.

After the present paper had been written, a series of communications appeared reporting interesting work on the stereochemistry of organophosphorus and organoarsenic compounds. Peerdeman et al.,[117] for the first time in the history of the stereochemistry of organoelementary compounds, have determined the absolute configuration of dextrorotatory benzylmethylphenyl-n-propylphosphonium bromide by X-ray examination, which has enabled absolute configurations to be determined for the optically active benzylmethylphenyl-n-propylarsonium and benzylmethylphenyl-n-propylammonium bromides[118].

Horner and Winkler[119] have determined by asymmetric synthesis the absolute configuration of dextrorotatory methylphenyl-n-propylphosphine. Horner and Balzer[120] have studied the stereochemical course of the reduction of optically active oxides of tertiary phosphines to the phosphines by means of trichlorosilane. Denney and Gershman[121] have taken the first step in studying the stereochemical course of the reaction of optically active methylphenylpropylphosphine with chloral. Horner and Hofer[122] have studied the dependence of the rate of racemisation of optically active quaternary arsonium salts on the chemical structure of the salts and the nature of the solvent, and have also put forward a new mechanism for this racemisation. Krawicki and Michalski[123] have resolved *O*-ethyl hydrogen ethylselenophosphonothioate by means of quinine.

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PROGRESS IN THE STUDY OF THE OXIDATION OF ORGANOMETALLIC COMPOUNDS

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1. INTRODUCTION

The chemistry of organometallic compounds has a history of more than one hundred years. Various organic compounds of zinc[1,2], boron[3,4], lead[5], and tin[6,7] were prepared as early as the middle of last century. A number of methods have now been developed, for the preparation of a variety of organic derivatives of a given metal, including those containing several atoms of different metals.

Considerable attention has been and is being paid to the study of the properties and reactions of organometallic compounds, since these compounds and their reactions are of considerable theoretical and practical interest. One of the most important reactions of organometallic compounds is their oxidation by oxygen and peroxides. It is well known that certain organometallic compounds, for example those of magnesium, zinc, and boron, are oxidised extremely readily by oxygen, but systematic studies in this direction were begun only in the last ten years.

Recent studies[8-15] have shown conclusively that the reaction of organometallic compounds with oxygen is accompanied by the formation of organometallic peroxides, which subsequently undergo various types of rapid conversion, including reaction with the original organometallic compounds. It has thus become necessary to study the reactions of organometallic compounds with various peroxides.

Systematic studies of the reactions of organometallic compounds with oxygen and peroxides are being carried out successfully in the USSR and abroad. The comprehensive, systematic, and detailed studies of Razuvaev are outstanding.

2. OXIDATION OF ORGANOMETALLIC COMPOUNDS WITH OXYGEN

Organometallic compounds differ extremely widely in their behaviour towards oxygen. Organic compounds of the alkali and alkaline-earth metals, zinc, cadmium, boron, aluminium, and titanium are often spontaneously flammable even at room temperature, whereas organic derivatives of germanium, tin, and lead have a high stability towards oxygen under ordinary conditions; organosilicon compounds are oxidised extremely slowly by oxygen even at elevated temperature.

The reactivity is undoubtedly influenced greatly by the energy of the metal–carbon and metal–oxygen bonds and by the electronic structure of the metal atoms in the organometallic compounds. In the reactions of these compounds with oxygen an important part may also be played by the formation of inorganic and organic peroxides and various complexes and associates, and also by temperature and the nature of the solvent.

It is not yet possible to put forward a fully substantiated single mechanism for the oxidation of all organometallic compounds by oxygen. This is due chiefly to the fact that there are no published data characterising quantitatively the influence of the above factors on the rate of the reaction of organometallic compounds with oxygen. For example, the energy of the metal–carbon bond is known only for a very small number of compounds[16]. Despite the difficulties, however, it is worth summarising the extensive information obtained by many workers on the oxidation of organometallic compounds by oxygen and trying to distinguish the characteristic features of the mechanism of these reactions. No one has yet undertaken this task, although the mechanism of the oxidation by oxygen of the organic compounds of certain metals, chiefly alkali metals, has been examined in a number of papers[17,18].

The oxidation of organometallic compounds by oxygen is a complex process involving several elementary chemical-conversion stages, the number of which depends on the specific conditions under which the reaction is carried out. Various intermediate or final stable products of the chemical transformation of organometallic compounds may be formed, depending on these conditions.

It is appropriate to consider first of all the oxidation by oxygen of those organometallic compounds which undergo this reaction very readily at room temperature or at even lower temperatures. The most characteristic feature of this group of compounds is that the formation of organometallic peroxides is much more rapid than their subsequent transformation. This relationship between the rates

of formation and decomposition of the organometallic peroxides makes it possible to use the reaction of organometallic compounds with oxygen to prepare various organic peroxo-compounds, and this is of interest in preparative chemistry.

It is assumed [14,19-21] that the first elementary step in the reaction of organometallic compounds with oxygen is the formation of an oxygen-containing complex:

$$RM + O_2 \rightleftarrows RM \cdot O_2 \qquad (1)$$

where M is a univalent metal atom and R an alkyl or aryl group.

The assumption that organometallic compounds form an oxygen-containing complex finds considerable justification in the fact that the organic compounds of many metals form stable complexes with ethers, amines, and certain other compounds. Moreover, in many cases very stable complexes consisting of the organic compounds of two different metals are formed.

The stability of the complex formed according to reaction (1) undoubtedly depends on a number of factors, particularly the nature of the original organometallic compounds. It is possible that under appropriate conditions these complexes will be fairly stable, and their dissociation to give the original products will take place slowly, so that their existence may somehow be proved. Some years ago an attempt was made to confirm experimentally the formation of a complex of this type in the oxidation of tri-n-butylboron with oxygen [20]. The results indicated unambiguously that the reaction mixture contained the stable complex $(C_4H_9)_3B \cdot O_2$. More careful experiments by other workers [22] showed convincingly, however, that the earlier results [20] were not reproducible and were therefore erroneous. Thorough examination of the results obtained by other workers in the study of the oxidation of organoboron compounds by oxygen leads to the conclusion that only unstable oxygen-containing complexes are formed in this reaction.

The complex formed may undergo subsequent rearrangement with formation of the corresponding organometallic peroxide [17]:

$$RM \cdot O_2 \rightarrow \begin{matrix} R^{-\delta} & O^{+\delta} \\ | & \cdot \; \| \\ M^{+\delta} & O^{-\delta} \end{matrix} \rightarrow \begin{matrix} R{-}O \\ | \\ M{-}O \end{matrix}. \qquad (2)$$

Rearrangement takes place in exactly the same way in the organometallic compounds of bivalent and tervalent metals:

$$R_2M \cdot O_2 \rightarrow RMOOR, \qquad (3)$$

$$R_3M \cdot O_2 \rightarrow R_2MOOR. \qquad (4)$$

We can represent the further oxidation of RMOOR, R_2MOOR, and $RM(OOR)_2$ in analogous fashion, with the formation of $M(OOR)_2$, $RM(OOR)_2$, and $M(OOR)_3$ respectively.

The formation of organometallic peroxides has been observed in the oxidation by oxygen of many organometallic compounds. As early as 1890 it was established that the reaction of diethylzinc with oxygen was accompanied by the formation of a peroxo-compound assumed to have the composition $C_2H_5ZnOOC_2H_5$. [23] In this case, however, the product was definitely not an organometallic peroxo-compound but a peroxo-compound of the diethyl ether used as solvent.

The oxidation by oxygen of the alkyl derivatives of the alkali and alkaline-earth metals, zinc, boron, and aluminium in a number of cases can be carried out in such a way that the yield of the resulting organometallic peroxides reaches 70-90%. [10,11] This makes it possible to use the reaction of organometallic compounds with oxygen to prepare alkyl hydroperoxides, which can be isolated from the reaction mixture after hydrolysis of the organometallic peroxides. This method sometimes has considerable advantages over other methods for the preparation of alkyl hydroperoxides.

Depending on the conditions of oxidation, the organometallic peroxides formed may subsequently undergo various transformations, particularly reaction with the original organometallic compound to form the alkoxide:

$$RM + MOOR \rightarrow 2MOR. \qquad (5)$$

The reaction of organic derivatives of bivalent and tervalent metals is analogous.

Organometallic peroxides may undergo not only intermolecular but also intramolecular reactions:

$$RMOOR \rightarrow M(OR)_2, \qquad (6)$$

$$R_2MOOR \rightarrow RM(OR)_2, \qquad (7)$$

$$RM(OOR)_2 \rightarrow (RO)_2MOOR, \qquad (8)$$

$$R(RO)MOOR \rightarrow M(OR)_3. \qquad (9)$$

It is next necessary to consider the possibility of reaction between the organometallic peroxides and the intermediate or final products of their transformation. Reaction in this case is accompanied by the rupture of carbon–carbon or carbon–hydrogen bonds. Finally, there is a definite probability of reaction between the organometallic peroxides and the solvent.

Thus a high yield of organometallic peroxides in the oxidation of organometallic compounds by oxygen can be obtained only when the reaction is carried out under definite conditions (low temperature, low concentration of oxidisable organometallic compounds, and relatively high oxygen concentration in the solution). These conditions are necessary in order that the rate of formation of the organometallic peroxides may exceed appreciably the rate of their transformation in a given direction.

The elucidation of regularities in the oxidation of organometallic compounds by oxygen might be facilitated considerably by kinetic studies of this reaction. Very few such studies have been made, so that information on the mechanism of the reaction of organometallic compounds with oxygen can be obtained only from papers giving the yields of the compounds formed when the reaction is carried out under certain conditions. In a number of cases these data are undoubtedly insufficiently reliable, since some of the products of the oxidation of organometallic compounds by oxygen, for example organometallic peroxides, are unstable compounds and their yield depends on the duration of the experiment.

The formation of organometallic peroxides in the reaction of the alkyl derivatives of metals with oxygen has been demonstrated by many workers, although in the great majority of cases the peroxo-compounds were not isolated from the reaction mixture. The situation is quite different for the oxidation by oxygen of aryl derivatives of metals. In this case attempts have been made to detect hydroperoxides or peroxides containing a peroxo-group directly attached to an aromatic radical, formed in the oxidation of the corresponding organometallic compounds [10,24]. However, no definite results have been obtained. It has been found [10] that the oxidation of phenylmagnesium halides, *p*-bromophenylmagnesium bromide, and mesitylmagnesium

bromide with oxygen in diethyl ether at -75° gives peroxo--compounds in yields amounting to 1–9% of the calculated quantity, but these compounds were not isolated from the reaction mixture and identified, and their presence was established only by iodometric titration.

Other workers [24] made a more thorough study of the oxidation of aryl compounds of lithium and magnesium, and established that the reaction of phenylmagnesium halides with oxygen in diethyl ether even at -120° takes place without the formation of peroxo-compounds. The oxidation of 9-anthryl-lithium in very dilute solution at -75° was accompanied by the formation of peroxo-compounds, hydrolysis of which gave 9.6 mole % of hydrogen peroxide and 14 mole % of an unidentified organic peroxide. The oxidation of anthrylmagnesium bromide with oxygen led to the formation of peroxo-compounds whose hydrolysis gave only hydrogen peroxide (12.5 mole %). [24]

Thus the results cited are not unambiguous, as the authors themselves point out. It may be suggested that the peroxo-compounds formed are oxidation products of the solvent. This suggestion is supported by the fact that benzoic acid was formed in the reaction of phenylmagnesium halides with oxygen; the benzoic acid is apparently a product of the oxidation of 1-phenylethanol, whose presence in the reaction mixture was also established. Hydrogen peroxide probably results from the hydrolysis of lithium peroxide or magnesium peroxide. The formation of these peroxides in the oxidation of the corresponding aryl derivatives with oxygen is quite possible, although unfortunately this possibility was not investigated in the works cited.

If the formation of organometallic peroxides took place only by reactions (1)–(4) and their transformation only by reactions (5)–(9), formation of hydrocarbons should not be observed in the oxidation of organometallic compounds by oxygen or air. However, the formation of hydrocarbons R–R and R–H has been observed repeatedly in these processes. For example, in the oxidation of phenyl-lithium with oxygen in benzene, biphenyl and lithium phenoxide were isolated in approximately equal quantities as the chief reaction products [25]. The oxidation of tolyl-lithium with oxygen in diethyl ether was accompanied by the formation of a number of compounds, including toluene and products of the dimerisation of tolyl radicals [26]. The formation of biphenyl was also observed in the oxidation by oxygen of phenylmagnesium bromide [27-29], diphenylmagnesium [30], diphenylzinc [30,31], diphenylmercury [32], and triphenylaluminium [33]. The yield of biphenyl depended to a marked extent on the reaction conditions, chiefly the nature of the solvent used. In the oxidation of phenylmagnesium bromide with oxygen in diethyl ether, benzene was formed in 10.6% yield. The oxidation of diphenylzinc with oxygen at room temperature was also accompanied by the formation of benzene, in 28% and 32% yield in cyclohexane and chloroform respectively. When the reaction was carried out in carbon tetrachloride, the product was not benzene but chlorobenzene, in 58% yield [31].

The formation of hydrocarbons in the oxidation of various organometallic compounds in the liquid phase by oxygen can readily be explained if we assume that this reaction takes place partly or entirely by a free-radical mechanism. Such a mechanism may involve the following elementary stages:

$$RM \cdot O_2 \longrightarrow R^{\cdot} + MOO^{\cdot}, \quad (10)$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}, \quad (11)$$

$$RM + ROO^{\cdot} \longrightarrow MOOR + R^{\cdot}, \quad (12)$$

$$RM + MOO^{\cdot} \longrightarrow MOOM + R^{\cdot}, \quad (13)$$

$$SH + R^{\cdot} \longrightarrow RH + S^{\cdot}, \quad (14)$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R_2, \quad (15)$$

$$R^{\cdot} + R^{\cdot} \longrightarrow RH + R_{-H}, \quad (16)$$

$$R^{\cdot} + S^{\cdot} \longrightarrow RS, \quad (17)$$

$$S^{\cdot} + S^{\cdot} \longrightarrow S_2. \quad (18)$$

Here SH represents the solvent or another compound present in the reaction mixture.

When R is an alkyl radical, reaction (11) takes place very readily with a low activation energy, so that in the oxidation of alkyl derivatives of metals, reactions (14)–(18) play a significant part only at very low concentrations of oxygen in the reaction mixture. Chain termination in the oxidation of alkyl derivatives of metals with oxygen takes place chiefly with the participation of peroxy-radicals.

If the rate of reaction (12) is much greater than the rate of reaction (13), the oxidation of an organometallic compound by oxygen gives chiefly the organometallic peroxide, not the metal peroxide.

The peroxo-compounds formed in reactions (12) and (13) may interact with the original organometallic compounds by reactions (5) and (19).

$$RM + MOOM \rightarrow MOM + ROM. \quad (19)$$

The situation is quite different when R is an aryl radical. Oxygen does not add on to aryl radicals with the formation of peroxy-radicals, so that reactions (14), (15), (17), and (18) play an important part in this case. The oxidation of these organometallic compounds by oxygen may involve the elementary stages (10), (13), and (20)–(27).

$$RM + MOO^{\cdot} \longrightarrow MOM + RO^{\cdot}, \quad (20)$$

$$RM + RO^{\cdot} \longrightarrow MOR + R^{\cdot}, \quad (21)$$

$$MOOM + R^{\cdot} \longrightarrow MOR + MO^{\cdot}, \quad (22)$$

$$RM + MO^{\cdot} \rightarrow MOM + R^{\cdot}, \quad (23)$$

$$MOO^{\cdot} + R^{\cdot} \longrightarrow RO^{\cdot} + MO^{\cdot}, \quad (24)$$

$$MO^{\cdot} + R^{\cdot} \longrightarrow MOR, \quad (25)$$

$$MO^{\cdot} + MO^{\cdot} \longrightarrow MOOM, \quad (26)$$

$$RO^{\cdot} + R^{\cdot} \longrightarrow ROR. \quad (27)$$

Chain termination in this case takes place by reactions (15) and (25)–(27), and may also take place by reactions (17) and (18), depending on the nature of the solvent. Confirmation of our assumption that reaction (17) is possible is provided by the formation of phenyltrichloromethane in the oxidation of diphenylzinc with oxygen in chloroform or carbon tetrachloride [31].

When a mixture of alkyl and aryl derivatives of a given metal is oxidised with oxygen, it is necessary to make allowance not only for the above stages but also for the possibility of reaction of the aryl organometallic compounds with an alkyl organometallic peroxide, and also with alkylperoxy-radicals. This is shown, for example, by the fact that the addition of alkylmagnesium halides to solutions of phenylmagnesium halides leads to a sharp increase in the yield of phenol in the oxidation of a mixture of these organometallic compounds with oxygen [34,35].

Reactions (19), (22), and (26) are characteristic only of the case where more or less stable metal peroxides are formed in the oxidation of aryl organometallic compounds by oxygen. In other cases, however, when these peroxides

are not formed, reactions (19), (22), and (26) must be excluded from the above scheme for the oxidation mechanism. This may be the case, for example, in the reaction of oxygen with aryl derivatives of boron and aluminium.

Some workers[18] conclude that the formation of hydrocarbons in the oxidation of organometallic compounds by oxygen results from the termolecular reaction

$$ROOM + 2RM \rightarrow ROM + MOM + R{-}R, \qquad (28)$$

but the following objections may be made to this conclusion. Firstly, there are no sufficiently convincing data on the formation of peroxides of the type ROOM in the oxidation of aryl organometallic compounds. Secondly the termolecular reaction (28) cannot explain the formation of hydrocarbons RH, although in a number of cases the formation of such compounds is an extremely characteristic feature. Thirdly and finally, reaction (28) makes no allowance for the participation of the solvent, despite the fact that a considerable number of studies have now established directly or indirectly that the solvent takes part in these processes. Thus the oxidation of tolyl-lithium with oxygen in diethyl ether leads to the formation of toluene and 1-tolylethanol[26]. In the case of phenylmagnesium bromide, formation of 1-phenylethanol was observed[27]. Phenol and biphenyl, formed in the oxidation of diphenylmagnesium with oxygen in deuterated benzene, contain deuterated phenyl radicals[30]. Similarly the oxidation of diphenylzinc in deuterated benzene gives deuterated biphenyl[30]. The same reaction in deuterated chloroform was accompanied by the formation of benzene containing 60% of deuterium[31].

These data indicate that in the oxidation of organometallic compounds by oxygen, hydrocarbons are formed not by reaction (28) but as a result of the formation of free radicals. An analogous conclusion was reached in a study of the products of the oxidation of trialkylborons in the liquid phase[36].

Kinetic studies of the oxidation of dimethylzinc, diethylzinc[37,38], triethylboron, and tri-n-propylboron[39] by oxygen in the gaseous phase also indicate a free-radical mechanism for this reaction.

The above chain mechanism for the oxidation of organometallic compounds by oxygen makes it possible to explain the fact that the alkyl derivatives of metals are more readily oxidised than the aryl derivatives. This difference is due chiefly to the marked tendency of alkyl radicals to react with oxygen with formation of the corresponding peroxy-radicals, and the complete absence of this tendency in aryl radicals. Therefore the oxidation of the readily oxidised alkyl organometallic compounds by oxygen takes place with the formation of a smaller number of reaction products than in the oxidation of the corresponding aryl organometallic compounds. Thus in the oxidation of dibutylzinc with oxygen in diethyl ether at 0° the yield of organometallic peroxide reached 90% of theoretical[11]. The oxidation of diphenylzinc with oxygen in cyclohexane, however, gives chiefly benzene, phenol, and biphenyl[31].

It is quite possible that the process may take place with the participation of free radicals or by molecular rearrangement of an oxygen-containing complex, depending on the specific conditions of the reaction. The ratio of the rates of these two processes may vary over a very wide range.

Papers dealing with the oxidation of organotitanium compounds by oxygen are particularly noteworthy. The chemistry of organotitanium compounds is still in the initial stage of its development (see, for example, a recently published review[40]). Systematic studies in this field are being successfully carried out by Razuvaev and his coworkers. It has been found that dicyclopentadienyltitanium[41], cyclopentadienylphenyltitanium[42], diphenyltitanium[43], and dicyclopentadienyldiphenyltitanium[41] are extremely readily oxidised by oxygen. It is significant that the rate of oxidation of dicyclopentadienyldiphenyltitanium depends to a marked extent on the nature of the solvent in which the reaction is conducted[41,44].

Other authors have also noted the extremely ready reaction of oxygen with dicyclopentadienyltitanium[45], trimethylcyclopentadienyltitanium[46,47], methyltitanium trichloride[48], ethyltitanium trichloride[48,49], and tetramethyltitanium[50].

The mechanism of the oxidation of organic compounds of mercury, silicon, tin, and lead differs significantly from that examined above. Here it should first of all be noted that the rate of oxidation of the organic compounds of these metals by oxygen depends to a very marked extent on the nature of the organic radicals present and also on the valency state of the metal atom. For example, the dialkyl and diaryl derivatives of tin[51-62] and lead[63-65], and the alkylated and arylated silanes[66-72] and stannanes[41,54,73-76], are readily oxidised by oxygen. The tetra-alkyl and more particularly the tetra-aryl derivatives of silicon, tin, and lead in most cases have a high stability towards oxygen, which decreases appreciably on going from the organic derivatives of silicon to the corresponding lead compounds. For example, tetraphenylsilicon is not oxidised appreciably when heated in air to 400°,[77] whereas tetraphenyl-lead inflames in air at a much lower temperature[78].

The influence of the nature of the organic radicals in the tetra-alkyl compounds of silicon, tin, and lead on the rate of the reaction of these compounds with oxygen is extremely marked. Replacement of primary alkyl radicals in a tetra-alkyl-lead by secondary alkyl radicals is accompanied by a significant increase in the rate of oxidation of these organolead compounds by oxygen[79,80]. Tetrabenzyl--lead is particularly readily oxidised by oxygen[81].

The oxidation of organomercury compounds by oxygen is of considerable interest. With a very early exception[82], no papers on these reactions have appeared until recently, since the opinion has long been held[83] that the organic compounds of mercury have a high stability towards oxygen. This incorrect opinion is convincingly refuted by the work of Razuvaev and his coworkers, which shows that in a number of cases organomercury compounds are very readily oxidised by oxygen. For example, dicyclohexylmercury in isopropyl alcohol is oxidised at a considerable rate even at room temperature[84]. Di-isopropylmercury[85-87], di-t-pentylmercury[86], and dibenzylmercury[86] show analogous behaviour.

A characteristic feature of the oxidation of dialkylmercury compounds by oxygen is the formation of a complex mixture of reaction products. For example, the oxidation of di-isopropylmercury by oxygen in carbon tetrachloride gave isopropylmercuric chloride, acetone, isopropyl chloride, chloroform, carbon monoxide, carbon dioxide, and metallic mercury[86]. This led to the suggestion that an organomercury peroxo-compound is formed[84,86] and that free radicals take part in the reaction of dialkylmercury with oxygen[86]. The suggestion that free radicals

are involved in the reactions of certain organomercury and organolead compounds with oxygen is confirmed by the results of a study of the nature of this process. The oxidation with oxygen of di-isopropylmercury[87] or tetraethyl-lead[88] shows a clearly defined induction period. Moreover, the addition of inhibitors decreases considerably the rate of reaction of di-isopropylmercury with oxygen[87].

A characteristic feature of the reaction of oxygen with alkyl compounds of mercury and metals in Group IVB of the Periodic System is the large temperature coefficient of reaction rate[87-90]; thus at low temperatures these reactions take place very slowly, and with increase in temperature several parallel and successive chemical processes take place simultaneously. With rise in temperature the peroxo-compounds formed undergo rapid reaction with the original organometallic compounds or with products of their transformation, so that it is very difficult to detect compounds containing peroxide oxygen in the reaction mixture.

If the organometallic compounds contain metal–metal bonds in addition to metal–carbon bonds, there is a marked increase in their reactivity. The rate of the reaction of these compounds with oxygen varies over a very wide range, depending on the nature of the metals forming the metal–metal bond. The reactions of this type of compound, including the reactions with oxygen, have been reviewed in detail[91].

3. OXIDATION OF ORGANOMETALLIC COMPOUNDS WITH PEROXIDES

The reactions of organometallic compounds with organic and inorganic peroxides are extremely numerous and varied, and in the past ten years a very large number of papers have been devoted to their study. The greatest contribution to the study of the reactions of organometallic compounds with peroxides has been made by Razuvaev and his coworkers, who have published a large number of papers reporting a systematic study of the reaction of the organic compounds of several metals with alkyl and acyl peroxides.

The character of the reaction of organometallic compounds with peroxides is influenced by the nature of the original compounds and the reaction conditions. These processes may take place by homolytic or heterolytic mechanisms. In a number of cases the mechanism is extremely complex.

The most characteristic heterolytic reaction of organometallic compounds with peroxides is nucleophilic substitution:

$$R_{n-1}MX + R'OOZ \rightarrow R_{n-1}MOOR' + XZ, \qquad (29)$$

where $n \geq 1$, M = metal, R = alkyl or aryl, R′ = metal, hydrogen, alkyl, or aryl, X = OH, NH_2, halide, alkyl, aryl, alkoxyl, aryloxy-radical, or some other substituent, and Z = metal or hydrogen. In a number of cases reaction (29) is reversible.

If M = mercury, silicon, germanium, tin, or lead and X = alkyl or aryl, reaction (29) takes place with great difficulty and extremely slowly. If the temperature is raised in order to increase the reaction rate, the organic compounds of these metals react with peroxides chiefly by a homolytic mechanism with rupture of the oxygen–oxygen bond.

Reaction (29) can be used to obtain a wide variety of organometallic peroxo-compounds, i.e. compounds containing both metal and peroxide oxygen. For example, the reaction of hydroperoxides with the oxides, hydroxides, alkoxides, hydrides, or amides of alkali and alkaline-earth metals gives the corresponding organometallic peroxides[92-102]. Peroxo-compounds are formed also by the reaction of hydroperoxides with dialkylzinc[12], dialkylcadmium[103], and trialkylaluminium[15]. Organometallic peroxides of boron[104], silicon[105-112], germanium[113,114], tin[114-116], and lead[114] are obtained by the reaction of hydroperoxides with organometallic compounds containing halogeno-, hydroxo-, or amino-groups joined to the metal.

If anhydrous hydrogen peroxide is used instead of hydroperoxides, it is possible to obtain metallo-organic peroxides. The difference between organometallic and metallo-organic peroxides is that the former contain a "carbon–peroxide oxygen" bond and the latter a "metal–peroxide oxygen–metal" bond.

All organometallic peroxo-compounds exhibit a number of common properties. In most cases they readily undergo hydrolysis and decompose rapidly in reactions with compounds containing labile hydrogen. All organometallic peroxo-compounds are powerful oxidising agents and very readily oxidise, for example, the organic compounds of a large number of metals, as noted in the first part of the present review.

A very interesting heterolytic reaction of organometallic peroxides is the intramolecular rearrangement of some of them:

$$R_3MOOCOR' \rightarrow R_2(RO)MOCOR'. \qquad (30)$$

There are sufficient grounds for assuming that the rearrangement takes place by a mechanism analogous to the familiar heterolytic rearrangement of peroxy-esters. This assumption is confirmed fairly convicingly by the results of a kinetic study of the heterolytic rearrangment of a number of acylperoxy-compounds of triphenyltin.

It was established that the product of reaction (30) in the case which we studied is readily hydrolysed by water:

$$C_6H_5O(C_6H_5)_2SnOCOR + H_2O \longrightarrow HO(C_6H_5)_2SnOCOR. \qquad (31)$$

The acyloxyhydroxydiphenyltin readily undergoes further transformation, owing to the ready disproportionation of the corresponding organotin compounds:

$$2\cdot HO(C_6H_5)_2SnOCOR \longrightarrow (C_6H_5)_2Sn(OH)_2 + (C_6H_5)_2Sn(OCOR)_2, \qquad (32)$$

$$(C_6H_5)_2Sn(OH)_2 \longrightarrow (C_6H_5)_2SnO + H_2O, \qquad (33)$$

$$2\cdot(C_6H_5)_2Sn(OCOR)_2 \longrightarrow (C_6H_5)_3SnOCOR + C_6H_5Sn(OCOR)_3, \qquad (34)$$

$$3\cdot C_6H_5Sn(OCOR)_3 \longrightarrow (C_6H_5)_2SnOCOR + 2Sn(OCOR)_4. \qquad (35)$$

The assumption that these disproportionations take place is convincingly confirmed by the results of a study of the composition of the reaction mixture formed under various hydrolysis conditions. Thus triphenyltin acetate was detected and isolated when aqueous diethyl ether was used for the hydrolysis of phenoxydiphenyltin acetate, which is in turn a product of the rearrangement of triphenyltin peracetate.

It might be suggested that the organotin compound formed by reaction (30) should react further with the peroxy-acid:

$$C_6H_5O(C_6H_5)_2SnOCOR + RCO_3H \rightarrow RCOO(C_6H_5)_2SnOCOR + C_6H_5OH. \qquad (36)$$

The organotin peroxo-compound newly formed by reaction (36) should, by analogy with reaction (30), have undergone transformation with the loss of peroxide oxygen. It was established, however, that this did not take place, and the yield of phenol never exceeded 1 mole per mole of original organotin compound.

Depending on the nature of the original organotin compound and the experimental conditions, the rate of formation of acylperoxytriphenyltin by the reaction

$$(C_6H_5)_3SnX+RCOOOH \rightarrow (C_6H_5)_3SnOOCOR+HX, \quad (37)$$

may be greater or less than the rate of reaction (30). The difference in the molecularities and hence in the orders of these reactions makes it possible to establish, from kinetic data, which of these processes is the slower.

If in the original organotin compound $(C_6H_5)_3SnX$ the substituent X is a hydroxo-, methoxy-, or nitrophenoxy--group, reaction (37) takes place very rapidly, and the rate of formation of the organotin compound $C_6H_5OSn(C_6H_5)_2OCOR$, containing no peroxo-group, is determined by the rate of reaction (30). On the other hand, if the substituent X in the original organotin compound is a chloro- or acyloxy--group, reaction (37) takes place much more slowly than the rearrangement of the organotin peroxo-compound formed from the starting materials. In this case the rate of formation of the acyloxyphenoxydiphenyltin, and hence the rate of decrease in the concentration of peroxo-compounds in the reaction mixture, is determined by the rate of reaction of the starting materials.

The rearrangement of organotin peroxo-compounds containing an acylperoxy-radical is a first-order reaction. The rate of this reaction depends to a marked extent on the nature of the organotin peroxo-compound, the nature of the solvent, and the temperature.

The rate of rearrangement of these compounds in anhydrous methanol increases with change in the radical R in $(C_6H_5)_3SnOOCOR$ in the sequence

$$CH_3 < n\text{-}C_6H_{13}C_6H_5 < C_6H_4NO_2\text{-}m\ (p) < C_6H_4NO_2\text{-}o.$$

The replacement of methanol by toluene leads to an increase in the rate of rearrangement of the acylperoxytriphenyltin. In methanol this reaction takes place at a high rate in the temperature range from -20° to 10°, whereas in toluene it takes place at approximately the same rate in the range from -30° to 0°.

In the reaction of triphenyltin acetate with peracetic acid in toluene, reaction (37) is much slower than reaction (30). This is quite understandable, since in the formation of triphenyltin peracetate a weak acid is displacing a stronger acid from its salt. The rate of decrease in the concentration of peroxo-compounds in the reaction mixture in this case is determined by the rate of the bimolecular reaction (37).

Acetic acid is liberated in the reaction of triphenyltin acetate with peracetic acid. It was found that the addition of acetic acid decreases considerably the rate of the reaction of peracetic acid with triphenyltin acetate in toluene. Study of the kinetics of this reaction shows that the free energy of activation increases regularly, while the entropy of activation decreases, with increase in the concentration of acetic acid in the reaction mixture.

It should be noted that the reaction of peracetic acid with triphenyltin acetate in toluene takes place at a measurable rate in the range 5–30°, where thermal decomposition of peroxycarboxylic acids is quite insignificant.

The rearrangement of various organic compounds of silicon[105], germanium[113], and lead[117] takes place in analogous fashion.

Interesting results were obtained in a study of the reaction of ethoxytriethyltin with benzoyl peroxide[118,119]. In an inert solvent, e.g. benzene, ethoxydiethyltin benzoate and ethyl benzoate are formed in 80–90% yield. It is suggested[118,119] that in this case the initial product is triethyltin perbenzoate, which subsequently undergoes the heterolytic rearrangement (30).

The spontaneous decomposition of organometallic peroxo-compounds by a homolytic mechanism is often accompanied by the formation of a complex mixture of chemical compounds. These compounds are products of the interaction of primary and secondary radicals with the solvent or with other substances present in the reaction mixture. The formation of free radicals during the spontaneous decomposition of organometallic peroxo-compounds is proved by the initiation of the polymerisation of various monomers as a result of the addition of, for example, organosilicon[105,106] and organotin[120-122] peroxides.

The reactions of organometallic compounds with organic peroxides in many cases also involves the participation of free radicals. The most interesting results on this type of reaction have been obtained by Razuvaev and his coworkers, who began to investigate the reactions of organometallic compounds more than thirty years ago. Even at that early date, in a study of the thermal decomposition of organic compounds of mercury, Razuvaev obtained the first evidence of the formation of free aryl radicals in solution[123-125]. Subsequent work proved the formation of free radicals in the thermal and photochemical decomposition of a number of organometallic compounds, for example in the thermal decomposition of diphenylmercury[123-127], tetraethyl-lead[128], and hexaethyldiplumbane[128], and also in the photochemical decomposition of dimethylmercury[129,130], diphenylmercury[21,131-135], and various other organic compounds of mercury[136-139].

Proof of the formation of free radicals in the thermal or photochemical decomposition of organometallic compounds was obtained using tracer atoms[21,126,127,133,134]. This method also provided proof that organic radicals of the organometallic compounds underwent exchange with the solvent.

Subsequently, Razuvaev and his coworkers found that oxygen and organic peroxides increase considerably the rate of decomposition of organometallic compounds and their exchange of organic radicals with the solvent[21,126]. This established the interrelationship of the thermal and photochemical decomposition of organometallic compounds with their oxidation by oxygen and peroxides.

Of the large number of homolytic reactions of organometallic compounds with peroxides, only those of alkyl and acyl peroxides with organic compounds of mercury[140], silicon[141-143], germanium[144], tin[142,143], and lead[141,142,145] have been studied in detail.

Benzoyl peroxide reacts with diethylmercury, di-isopropylmercury, and diphenylmercury[140] with the formation of a complex mixture of products, probably resulting from simultaneous molecular and free-radical processes.

The reaction of di-isopropylmercury with t-butyl hydroperoxide takes place fairly readily. It is suggested

that this reaction involves the intermediate formation of an organomercury peroxo-compound.

Tetra-alkyl derivatives of silicon, germanium, tin, and lead react readily at 80–95° with acyl peroxides, the direction of the reaction depending to a marked extent on the metal. Thus in the reaction of benzoyl peroxide with tetraethylsilane [141,142] and hexaethyldisilane [143] no rupture of the Si–C bond is observed, whereas the reaction with tetraethylgermanium gives products which indicate rupture of the Ge–C bond [144]. This is shown to an even greater extent in the reactions of acyl peroxides with tetraethyltin [142] and tetraethyl-lead [141,142], and also with hexaethyldistannane [142] and hexaethyldiplumbane [145]. The reaction at 130–150° of t-butyl peroxide with tetraethylgermanium [144], tetraethyltin [142], and hexaethyldistannane [143] is to some extent analogous.

The experimental results indicated that the reactions of acyl and alkyl peroxides with alkyl derivatives of mercury, silicon, germanium, tin, and lead take place either completely or partly by a free-radical mechanism.

The formation of free radicals in the oxidation of organometallic compounds by oxygen or peroxides can be used to initiate various chain reactions. Among these reactions, radical polymerisation is of particular interest. The most important results in this connection have been obtained in the study of polymerisation initiated by organoboron and organoaluminium compounds in the presence of oxygen or peroxides.

It is now firmly established that trialkylborons in the presence of oxygen are powerful initiators of the radical polymerisation of many unsaturated compounds. The first papers on the study of organoboron compounds as initiators for the polymerisation of unsaturated compounds were published in 1957 [146–149]. These were followed by others [150–158] containing more or less detailed information on the initiating power of various trialkylborons and the mechanism of the reactions taking place.

It was first found that tributylboron initiates the polymerisation of acrylonitrile [146,149], methyl methacrylate [147,149], ethylene [148], styrene [147,149], vinyl chloride, vinyl acetate, and n-butyl vinyl ether [149]. It was established that the emulsion polymerisation of acrylonitrile at 20° and 50° in the presence of tributylboron takes place only if oxygen is also present [150]; it was shown that peroxo-compounds of the type R_2BOOR, $RB(OOR)_2$, or $B(OOR)_3$ are formed. The addition of isobutyldi-isobutylperoxyboron to acrylonitrile brings about polymerisation of the latter [159], indicating homolytic dissociation of this organoboron peroxo-compound.

It has been suggested [153,155–158] that the mechanism of polymerisation initiation is more complex than oxidation of the trialkyborons by oxygen to the corresponding peroxides followed by their homolytic dissociation. It was first suggested that a complex $R_3B.O_2$ is formed and acts as polymerisation initiator [155], but, as already noted, if this complex is formed at all, it may well undergo rapid rearrangement to a more stable peroxo-compound or decompose to the original components.

Published data on the part played by organoboron peroxides in the initiation of radical polymerisation are contradictory. It has been shown [159] that the initiating power of isobutyldi-isobutylperoxyboron is the same as that of tri-isobutylboron in the presence of air, yet it has also been stated [156] that neither tri-n-butylboron nor its peroxide is by itself an effective initiator for the polymerisation of methyl methacrylate, but that when taken together these compounds are extremely active. On this basis it was suggested that the initiation involves the stages

$$R_3B+M \rightleftarrows R_3B\cdot M, \qquad (38)$$

$$R_3B\cdot M+R_2BOOR \rightarrow R_3B\cdot M\cdot RO^{\cdot}+R_2BO^{\cdot}, \qquad (39)$$

where M represents a molecule of the monomer.

Study of the influence of the $[R_3B]:[O_2]$ ratio on the degree and initial rate of polymerisation showed that the process takes place most readily when this ratio is close to unity [158]. When $[R_3B] \ll [O_2]$, all the organoboron compound is converted into the peroxide, whereas when $[R_3B] \gg [O_2]$ the peroxide formed is very rapidly used up in the reaction with R_3B, so that the polymerisation is rapidly quenched. Here, as before [156], it is suggested that the formation of radicals takes place readily only by reaction of the trialkylboron with its peroxide.

The role of oxygen in polymerisation initiated by a trialkylboron can be played by various other oxygen-containing compounds — hydrogen peroxide, manganese dioxide, copper(II) oxide, etc. [153]

Organoaluminium compounds, like organoboron compounds, initiate radical polymerisation in the presence of oxygen or peroxides. The initiation of the polymerisation of various monomers by a trialkylaluminium has been studied by a number of workers [160–167]. It has been established [161] that the polymerisation of vinyl chloride, initiated by triethylaluminium in the presence of oxygen, involves an induction period. The existence of the induction period was attributed to preliminary oxidation of the original organoaluminium compound by oxygen. This reaction gives compounds containing oxide and peroxide oxygen, introduced at the "aluminium–carbon" bond. These organoaluminium peroxo-compounds react more or less readily with organoaluminium compounds still containing unoxidised "aluminium–carbon" bonds. This stage [161] also determines the initiating power of the "trialkylaluminium–oxygen" system. Instead of trialkylaluminium compounds, it is possible to use for this purpose alkylalkoxyaluminium compounds with varying degrees of replacement of alkyl radicals by alkoxy-radicals. Study of the initiating power of these compounds for the particular case of ethyl derivatives of aluminium showed that, in the presence of oxygen, diethylaluminium ethoxide is a most active initiator for the polymerisation of vinyl chloride.

The influence of the nature of the alkyl radicals in trialkylaluminium on the initiating power in the presence of oxygen has also been studied [163]. It was concluded that the organoaluminium compounds bring about radical polymerisation only under conditions which ensure their conversion into corresponding peroxo-compounds.

The initiating activity of trialkylaluminium compounds in the presence of organic peroxides has been studied [162,163,168].

Triethylaluminium reacts vigorously even at 0° with cumenyl hydroperoxide [163] with the liberation of ethane and the formation of an organoaluminium peroxo-compound, which undergoes further transformation more or less rapidly depending on the reactant concentrations.

The "triethylaluminium–cumenyl hydroperoxide" system does not effectively initiate the polymerisation of vinyl acetate. If diethylaluminium ethoxide is used instead of triethylaluminium, the system is an effective initiator for

the polymerisation of this monomer. If ethylaluminium diethoxide is used instead of diethylaluminium ethoxide, a considerable decrease in initiating power is observed.

The systems formed by triethylaluminium and tri-isobutylaluminium with benzoyl peroxide are effective initiators for the radical polymerisation of vinyl acetate, methyl methacrylate, and acrylonitrile[162,168]. It was found that these initiators bring about polymerisation of the monomers even at -30°. Replacement of an alkyl derivative of aluminium by an alkoxy-derivative is accompanied by complete loss of initiating power in the presence of benzoyl peroxide.

A kinetic study has been made[168] of the polymerisation of vinyl acetate initiated by triethylaluminium in the presence of benzoyl peroxide.

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TRANSESTERIFICATION OF PHOSPHITES AND PHOSPHONITES WITH MONOHYDRIC AND POLYHYDRIC ALCOHOLS AND PHENOLS

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I. INTRODUCTION

Twenty years ago the chemistry of the organic compounds of phosphorus entered a period of vigorous development. About a hundred years were required, after the first organophosphorus compounds had been prepared, for sufficient experimental results to accumulate and for the theoretical and practical value of certain compounds to be assessed, which determined the further development of this branch of organic chemistry. The most important work, which provided a foundation for further investigations, was undertaken by Michaelis, Arbuzov, and their many students.

At the present time the practical application of organophosphorus compounds is being continually extended. Because of their high thermal and chemical stability they are successfully employed as plasticisers for synthetic resins, on which they confer non-flammability, resistance to frost[1-3], and sometimes stability towards radiation[4]. The use of organic compounds of phosphorus as extractants[5,6] and flotation agents[7] is no less valuable. Substances containing phosphorus have proved to be valuable additives for lubricating oils, giving to the latter durability and several other desirable properties[8]. Polymers and oligomers containing phosphorus are used for the manufacture of ion-exchange resins, surface-active agents, adhesives, glasses with unique optical properties, etc.[9]

A large number of physiologically active substances of practical interest have been found among organophosphorus compounds. The chemistry of phosphorus occupies a primary place in the number and variety of pesticides. The products Thiophos, Chlorophos, Carbophos, Octamethyl, Butaphos, Ragor, Systoxes, etc. have received wide publicity, and are used in large quantities in agriculture.

Organophosphorus poisons, discovered during recent decades, are more toxic than all hitherto known poisons, and in this respect approach the most virulent compounds of vegetable and animal origin.

Organophosphorus compounds are used also as drugs, e.g. in the treatment of glaucoma (Phosarbin, Armin, Fosfakol)[10], tumours (TEPA, Thio-TEPA, DIPIN, etc.)[11,12], and cardiovascular diseases (hydrazides and amides of thiophosphates)[13]. Natural substances containing phosphorus – nucleic acids, phosphatides, coenzymes, glycopyrophosphates, and many others – are extremely important for the vital activity of organisms[14].

The organophosphorus compounds which find practical use or which are of importance in biochemical processes are mainly esters and amide–esters of phosphoric, phosphorothioic, and pyrophosphoric acids, derivatives of alkylphosphonic acids, and phosphine oxides. It is essentially the chemistry of phosphates and pyrophosphates which is of concern to industry and biochemistry. The importance of phosphates, phosphorothioates, and pyrophosphates is determined not only by their usefulness but also by their availability.

A common feature of several methods of obtaining these compounds is the use of acid and normal phosphorous esters as intermediates in their synthesis. Thus various phosphates are obtained by oxidising phosphites by the addition of sulphur to them, chlorination, reaction with sulphur chlorides, disulphides, thiocyanates, sulphenyl chlorides, chloramines, etc. The alkylation of sodium phosphites by Michaelis' method and of normal phosphites by Arbozov's method or the addition of dialkyl phosphites to unsaturated compounds, etc. yields phosphonates.

Thus phosphites, while being of intrinsic value in their use as such, possess high reactivity, and are therefore

key materials for the preparation of various organic compounds of phosphorus. However, the synthesis of phosphites by the reaction of alcohols with phosphorus trichloride often gives poor yields of the desired products, and sometimes leads to negative results, especially in the preparation of esters containing acid-labile groups. A good method for the synthesis of esters is transesterification, which is widely known in organic chemistry. Its application to the chemistry of carboxylic esters has especially varied aspects, and it has been studied in detail in the preparation of these compounds. The reaction occurs under comparatively mild conditions, is not accompanied by the liberation of corrosive products, and gives good yields of the required materials, so that it is often employed in the preparation of vitamins[15], proteins[16-18], lipids[19,20], and other labile compounds[21,22]. Alcoholysis of esters of dibasic and polybasic acids with glycols and polyols is employed for the synthesis of polymeric compounds[23]. For example, lavsan (Terylene) is obtained by the interaction of dimethyl terephthalate with ethylene glycol.

Study of transesterification has shown that, as a rule, the alkoxy-group of the ester is replaced by an alcohol radical of higher molecular weight. In some cases this does not apply: esters formed by phenols, glycol, glycerol, and some other hydroxy-compounds having enhanced acidic properties are transesterified by simple alcohols[21,24-26]. The presence of a double bond in the $\alpha\beta$-position to the alkoxycarbonyl group of the initial ester hinders transesterification[21,27,28], while the presence of electrophilic groups (phenyl, acetyl, acetoxyl, carboxyl, nitrile, carbonyl) favours alcoholysis[21,29-34]. Transesterification is accelerated by the addition of mineral acids[33,35], sodium alkoxides[36-39], and in isolated cases pyrophoric lead[40], oxides of magnesium and lead, and acetates of cadmium, zinc, and cobalt or a mixture of the oxides and acetates of these metals[41].

Esters of boric[42], silicic[43-46], titanic[47-49], antimonous[50], arsenious[51,52], and phosphoric acids also undergo transesterification, but considerably less work has been done on these reactions.

II. TRANSESTERIFICATION OF NORMAL PHOSPHITES

Esters of acids containing tervalent phosphorus readily undergo transesterification, which involves all or only some of the ester groups depending on the conditions, the structure of the initial reactants, and especially the proportions of the latter. In the former case symmetrical esters are produced, and in the latter mixed esters:

$$(RO)_3P + 3R'OH \longrightarrow (R'O)_3P,$$
$$(RO)_3P + 2R'OH \longrightarrow (R'O)_2POR,$$
$$(RO)_3P + R'OH \longrightarrow (RO)_2POR'.$$

The most detailed study of the reaction has been made on the alcoholysis of triethyl phosphite.

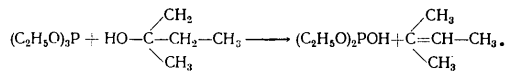
The exhaustive transesterification of triethyl phosphite was first studied by Arbuzov and Vinogradova: with a phosphite : alcohol molar ratio close to 1 : 3–4 in the presence of orthophosphoric acid, they obtained 30–50% yields of trihexyl, trioctyl, trinonyl, trihexadecyl, and tricyclohexyl phosphites[53]. The relatively low yield of products of complete transesterification is explained by the formation, with the above relative proportions of the reactants, of considerable quantities of mixed phosphites. This was subsequently confirmed by other investigators, who conducted the reaction in the presence of sodium alkoxides[54]. Even with a phosphite : alcohol ratio exceeding 1 : 5, unsymmetrical phosphites were detected among the reaction products[53-56]. With a ratio of 2 : 1 the reaction can be halted[55] at the first stage, i.e. at the formation mainly of monosubstituted products.

The mixed phosphites $(RO)_2POR'$ which are thus formed can react with another alcohol to form phosphites containing three different alkoxy-groups[54]:

$$(RO)_2POR' + HOR'' \longrightarrow (RO)(R'O)(R''O)P.$$

Derivatives of the lower alcohols are unstable and readily disproportionate on distillation. Mixed esters containing residues of higher alcohols are more stable to disproportionation: butyl dihexyl phosphite remains practically unchanged on distillation[54].

The character of the transesterification is greatly influenced by the structure of the initial alcohol. Whereas the alcoholysis of trialkyl phosphites by primary and secondary alcohols proceeds normally, diethyl hydrogen phosphite and 2-methylbut-2-ene have been isolated from the reaction between triethyl phosphite and t-pentyl alcohol[55]:

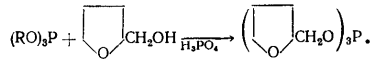


It was not established whether initial partial transesterification to diethyl isopentyl phosphite was followed by decomposition of the latter into the alkene and diethyl hydrogen phosphite, or whether the initial alcohol was dehydrated and the initial phosphite hydrolysed.

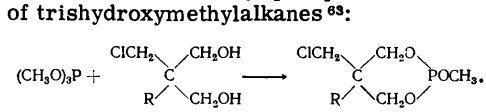
Alcoholysis by alcohols containing electronegative substituents (2,2,2-trichloroethanol, 2,2,2-trifluoroethanol) is extremely sluggish: with the latter alcohol only 4% of the monotransesterification product can be isolated[55]. This process goes considerably better with 2-alkylthioethanols, which possess less acidic hydroxyls[57-59]:

$$(RO)_3P + HOCH_2CH_2SR' \longrightarrow (RO)_2POCH_2CH_2SR'.$$

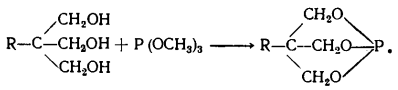
while with tetrahydrofurfuryl alcohol the product of complete transesterification is obtained in good yield[60]:



Trialkyl phosphites are transesterified not only by monohydric but also by polyhydric alcohols. However, few relevant data are available, and these are not soundly based. For example, it has been suggested that the use of glycol yields polyesters[61,62], although the conditions of the synthesis are not cited, and no evidence is given for the structure of the products. It is quite possible that in this case cyclic phosphites were obtained, as in the transesterification of trimethyl phosphite with monochlorohydrins of trishydroxymethylalkanes[63]:



Trialkyl phosphites react with trishydroxymethylalkanes themselves to form products of complete transesterification — bridged cyclic phosphites — which it is difficult to prepare by other methods[63]:



Phosphites are not transesterified by thiols, with which they interact to form hydrocarbons and phosphorothionates[64-66]:

$$RSH + P(OC_2H_5)_3 \longrightarrow RH + S{=}P(OC_2H_5)_3.$$

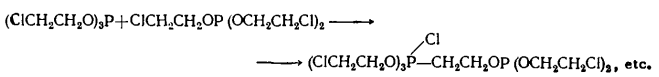
The reaction is catalysed by free radicals, and probably proceeds by a radical mechanism:

$$RS\cdot + P(OC_2H_5)_3 \longrightarrow RS{-}\dot{P}(OC_2H_5)_3,$$
$$RS{-}\dot{P}(OC_2H_5)_3 \longrightarrow R\cdot + S{=}P(OC_2H_5)_3,$$
$$R\cdot + HSR \longrightarrow RH + RS\cdot.$$

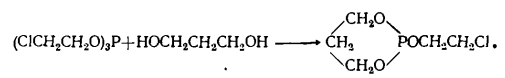
Benzenethiol reacts with triethyl phosphite to form diethyl hydrogen phosphite and ethyl phenyl sulphide[65]:

$$C_6H_5SH + P(OC_2H_5)_3 \longrightarrow C_6H_5SC_2H_5 + HOP(OC_2H_5)_2.$$

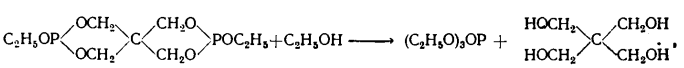
Phosphites of more complicated structure are also capable of undergoing transesterification. It has been stated that tris-2-chloroethyl phosphite can be completely transesterified more readily than triethyl phosphite with 2-ethylhexanol and benzyl alcohol even in the absence of a catalyst[62,67], but concrete data on the yields of the final products of alcoholysis are lacking. It was reported[67] that transesterification was accompanied by alkylation of the tris-2-chloroethyl phosphite with formation of a mixture of difficultly separable products:



Reaction of tris-2-chloroethyl phosphite with propane-1,3-diol leads to the formation of a cyclic phosphite[68]:



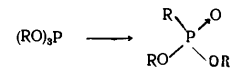
Another example of the alcoholysis of a complex phosphite is the transesterification of the dicyclic ester formed by pentaerythritol with two molecules of ethyl dihydrogen phosphite



which also occurs under milder conditions than with simple phosphites[69].

The transesterification of triaryl phosphites has been studied mainly on the reactions of triphenyl phosphite with monohydric alcohols, glycols, and polyhydric phenols. This reaction also occurs in stages, but under milder conditions than with trialkyl phosphites.

The earliest data on the possibility of transesterifying esters of acids containing phosphorus were obtained in 1917 by Milobendzki and Szulgin using triphenyl phosphite[70]. These workers first tried to transesterify triphenyl phosphite with methanol and propanol by heating in glass tubes, but obtained negative results: under the experimental conditions the trialkyl phosphites formed isomerised into alkylphosphonates:



The complete transesterification product could be obtained only by using the alkoxides instead of the alcohols[70]:

$$(C_6H_5O)_3P + 3RONa \longrightarrow (RO)_3P + 3C_6H_5ONa.$$

Considerably later, a communication appeared on the preparation of trimethyl and triethyl phosphites by complete transesterification of triaryl phosphites with alcohols[71]. It was remarked that the reaction goes smoothly in the presence of calcium or lead oxide, or sodium phenoxides or alkoxides. According to results obtained by the present Reviewers, the transesterification of triaryl phosphites with methanol and ethanol yields a difficultly separable mixture of products[72]. Satisfactory (60–99%) yields of the complete transesterification products are achieved only by using alcohols containing six or more carbon atoms and 2-naphthol.

The partial transesterification of triaryl phosphites has been studied more thoroughly[73-76]. Alkyl diaryl phosphites have been obtained by the reaction of triphenyl and tritolyl phosphites with butanol, octanol, hexadecanol, and cyclohexanol in equimolecular proportions. Mixed phosphites containing higher alkyl radicals, e.g. hexadecyl, have found application as antioxidants for lubricating oils[73,74].

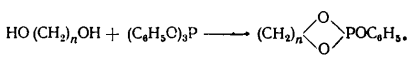
Triaryl phosphites are readily transesterified by various substituted alcohols, the completeness of the transesterification being found to depend on the proportions of the reactants. When allyl and 2-methylallyl alcohols are used with a phosphite : alcohol ratio close to 1 : 6, trialkenyl phosphites are obtained[77]:

$$(C_6H_5O)_3P + HOCH_2CH{=}CH_2 \longrightarrow (CH_2{=}CH{-}CH_2O)_3P.$$

At lower concentrations of the alcohol mixed alkenyl aryl phosphites are observed in the reaction products. Alcoholysis of triaryl phosphites (one mole) with aminoalkanols (one equivalent) yields partly substituted products[78]:

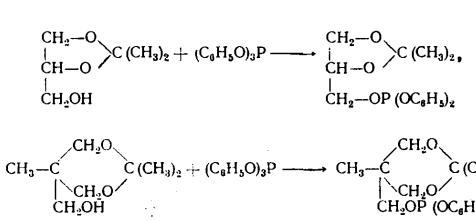
$$3(C_6H_5O)_3P + (HOCH_2CH_2)_3N \longrightarrow [(C_6H_5O)_2POCH_2CH_2]_3N.$$

Triphenyl phosphite reacts with glycols to form cyclic phosphites[79]:



With glycols in which the hydroxyls were well separated ($n > 5$) polymeric products were formed, but were not characterised.

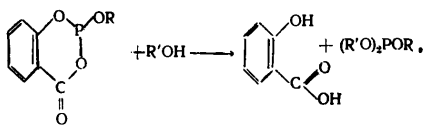
Transesterification of triphenyl phosphite with the isopropylidene derivatives of glycerol and metriol in equimolecular proportions gives high yields of the isopropylidenedioxyalkyl diphenyl phosphite, only one ester group of the phosphite being transesterified[80]:



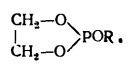
Reaction of triphenyl phosphite with cellulose at 130–135° yields a phosphorylated cellulose containing up to 5–6% of phosphorus[81].

When dihydric and trihydric phenols are used in this reaction, good yields are obtained of cross-linked or branched poly(arylene phosphites)[82]. The phenolic components used were quinol, 2,2-diphenylpropane-*pp'*-diol, and benzene-1,2,4-triol. Phenolysis occurred quite readily, and was accompanied by separation of almost the theoretical quantity of phenol. The presence of catalysts has little influence on the transesterification or the quality of the polymers. Poly(arylene phosphites) of network structure form an infusible, stable vitreous mass, which is insoluble in organic solvents.

Alkyl salicyloyl phosphites react with alcohols to form a mixed trialkyl phosphite and salicylic acid[83]:



The first stage probably involves cleavage of the anhydride link with formation of an *o*-dialkoxyphosphino-oxybenzoic acid, after which the aromatic radical of the phosphorous ester undergoes transesterification. The reaction goes vigorously with ethanol, isopentyl alcohol, and ethylene glycol, with formation in the last case of a cyclic ester



III. TRANSESTERIFICATION OF ACID PHOSPHITES

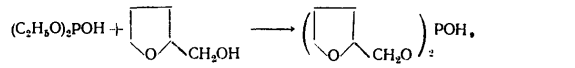
Dialkyl and diaryl phosphites, like normal phosphites, are transesterified by monohydric alcohols, glycols, and polyhydric phenols. The reaction occurs in stages (complete and partial), and can be terminated at the formation of unsymmetrical phosphites.

The complete transesterification of dialkyl phosphites was used for the first time by Arbuzov and Vinogradova for the synthesis of higher dialkyl phosphites[43]. With a phosphite : alcohol molar ratio of 1 : 2 in the presence of orthophosphoric acid they obtained symmetrical dialkyl phosphites mixed with considerable quantities of unsymmetrical phosphites, resulting from partial alcoholysis.

Interaction of dialkyl phosphites with cyclohexanol, benzyl alcohol, octan-2-ol, and ethylene glycol gave a complex mixture, from which pure substances could not be isolated. It was later found that the formation of transesterification products is accelerated in the presence of alkaline catalysts and an increased molar ratio of alcohol to phosphite[84–86]. With a phosphite : alcohol ratio of 1 : 3 in the presence of sodium ethoxide, symmetrical dialkyl phosphites were obtained in yields of 70–90%.[83]

The complete transesterification of dialkyl phosphites by aliphatic alcohols goes smoothly in xylene (with yields up to 85%) and in the absence of a catalyst[87]. Bis-2-ethylhexyl and bis-2-chloroethyl phosphites have been obtained in this way; in the presence of orthophosphoric acid without a solvent the yield of the latter is only 43%.[88]

Transesterification of diethyl phosphite with tetrahydrofurfuryl alcohol and 2-methoxyethanol in the presence of sodium gave the complete substitution products in yields of 44%[89] and 60.5%:[88]



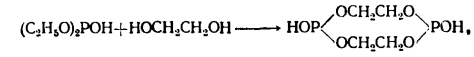
$$(C_2H_5O)_2POH + CH_3OCH_2CH_2OH \longrightarrow (CH_3OCH_2CH_2O)_2POH.$$

When diethyl phosphite was treated with β-hydroxypropionitrile in proportions of 1 : 3 in the presence of phosphoric acid, a 30% yield of the product of complete transesterification was obtained[88]. The reaction of phosphorus trichloride with β-hydroxypropionitrile results in a complex mixture of products, which it is almost impossible to separate[90].

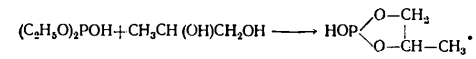
Complete replacement of alkoxy-groups has been reported in the transesterification of simple dialkyl phosphites with alcohols containing ethylenic and acetylenic bonds[91]. The reaction of bis-2-chloroethyl phosphite with 2-ethylhexan-1-ol occurs similarly[87]. Alcoholysis of dialkyl phosphites occurs more readily the more strongly electrophilic the substituents in their ester groups. Thus diethyl phosphite is transesterified by decanol at 160–170°, bis-2-chloroethyl phosphite at 140–150°, and bis-2-fluoroethyl phosphite at 120–130°.[88] With equimolecular proportions of the reactants in the presence of orthophosphoric acid or sodium ethoxide, or in the absence of a catalyst, mixed dialkyl phosphites are formed in yields of 24–45%.[43,85,92]

Unsymmetrical phosphites can be used to obtain various unsymmetrical esters of phosphoric and phosphonic acids[93], individual representatives of which possess physiological activity.

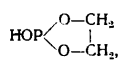
The transesterification of dialkyl phosphites with glycols is of great interest. Several papers have been published on the reactions of diethyl hydrogen phosphite with ethylene glycol, but results obtained by different investigators are mutually contradictory. It has been reported[68] that in the presence of sodium a bisphosphite containing a ten-membered ring is obtained:



while with other glycols, in particular propane-1,2-diol, a phosphite containing a five-membered ring is formed:

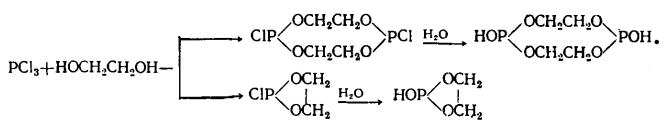


Several other papers suggest that the transesterification of dialkyl phosphites with glycols, mainly ethylene glycol (under similar conditions), yields polymeric products[94–96]. In no case, however, is any evidence given for the structure of the substances which are formed. Nevertheless, we cannot exclude the formation, in the transesterification of diethyl phosphite with a glycol, of a linear bisphosphite — the partial transesterification product $C_2H_5OP(OH).OCH_2CH_2OP(OH)OC_2H_5$ — and the five-membered cyclic phosphite



which are similar in composition to the ten-membered cyclic bisphosphite. The linear bisphosphite is unknown;

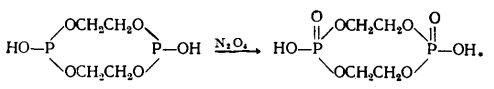
cyclic mono- and bis-phosphites have previously been obtained from the same starting materials under analogous conditions[97-103], and their structures have also not been proved:



It has subsequently been shown, as a result of a detailed study of this reaction[104], that, with equimolecular proportions of diethyl phosphite and glycol in the presence of sodium at 135–140° (200 mm) a substance is obtained which distils almost completely under vacuum. Elementary analysis and molecular weight determination† show it to correspond to a ten-membered cyclic bisphosphite.

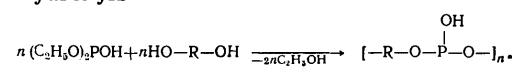
The same product is obtained by the action of ethylene glycol on bis-2-chloroethyl phosphite.

On oxidation with nitrogen dioxide the cyclic bisphosphite is converted into the corresponding bisphosphate, which can be titrated as a dibasic acid:



Polyesters containing two or three residues of the starting materials are formed when diethyl phosphite is transesterified with di-, tetra, and hexa-ethylene glycols, propylene glycol, butane-1,3-diol, butane-1,4-diol, but-2-yne-1,4-diol, and bis-2-hydroxyethylamine[96].

Polyphosphites of high molecular weight are readily formed by the reaction of diethyl phosphite and other simple dialkyl phosphites with glycols which either possess spatially isolated hydroxyls or are unstable in conformations with adjacent hydroxyls[105,106]:



Positive results were obtained with the following glycols — pentane-1,5-diol, hexane-1,6-diol, diethylene glycol, triethylene glycol, diethanols, pentafluoropentane-1,5-diol, 1,4:3,6-dianhydrosorbitol, *p*-bishydroxymethylbenzene, and 2,2-bischloromethylpropane-1,3-diol — but polyphosphites could not be obtained with 1,4-diols, dehydration of the glycol probably occurring in this case with the formation of tetrahydrofuran.

Polyphosphites were synthesised by heating an equimolecular mixture of the reactants with a catalytic quantity of metallic sodium in a stream of an inert gas at 130–150°,

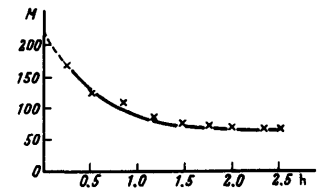


Fig.1. Dependence of molecular weight *M* of diethylene bisphosphite on time of storage of the solution .

first at atmospheric pressure and then at reduced pressure (200 mm). Reaction was complete in 5–6 h. It is considerably more difficult to transesterify phosphites with 1,4:3,6-dianhydrosorbitol and pentafluoropentane-1,5-diol. This is probably due in the first case to the use of a secondary alcohol, and in the second case to the fact that the glycol is considerably more acidic than the other diols. Better results are obtained in the transesterification of bis-2-chloroethyl phosphite.

The polyphosphites obtained are thick liquids or vitreous materials, faintly yellowish, and soluble in most polar organic solvents; polyphosphites containing a heteroatom in the alkylene radicals are soluble in water. An exception to this rule is provided by the polyphosphite obtained from *p*-bishydroxymethylbenzene, which dissolves in no known solvent. This polymer is distinguished also by high thermal stability: under conditions of prolonged heating it begins to change only at 300–500° (Fig. 2).

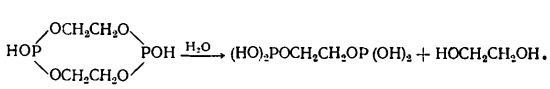
The linear polyphosphites had molecular weights of $23-150 \times 10^3$ determined by light scattering.

As the excess of glycol in the reaction mixture is increased, polymers of lower specific viscosity are formed on transesterification. The regular fall in viscosity of the products is probably due to the formation of oligomers under the given conditions.

Thus the transesterification of dialkyl phosphites with glycols is a convenient method of synthesising polyphosphites. From the point of view of practical application, however, the method has the disadvantage that many glycols are still relatively difficult to obtain. It is therefore of interest to use the readily accessible polyols — glycerol and pentaerythritol[106,107].

The molecular weights of the polyphosphites obtained do not usually exceed 1000–1500, probably owing to contamination of the polyesters with cyclic phosphites of the polyols. On prolonged storage and heating, the cyclic esters are converted into polymeric compounds, since the specific viscosities of the solutions are greatly increased.

† The molecular weight was determined cryoscopically in water. Its value depends on the time of storage of the solution, the maximum of 220 (found by extrapolation) falling to 60 and then remaining unchanged for a long time (Fig. 1). This is probably explained by hydrolysis of the cyclic bisphosphite:



Titration of the hydrolysis product showed that a dibasic acid had been formed.

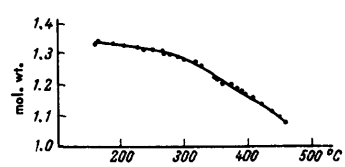
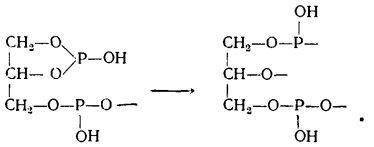


Fig.2. Thermal stability of poly-(*p*-xylylene phosphite).

Thus the product obtained from glycerol and diethyl phosphite, for example, having a specific viscosity of 0.36, has almost double this viscosity after storage for 2 months; after heating at 175–180° for 10 h the viscosity rises to 0.50, and for 20 h to 0.74.



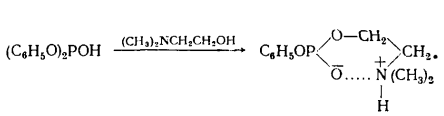
Transesterification of diethyl phosphite with cellulose in the presence of sodium at 160–165° yields a cellulose phosphite containing up to 6.4% of phosphorus[81].

Poly(arylene phosphites) have been obtained by the transesterification of dialkyl phosphites with dihydric phenols[106,108–110].

The transesterification of diaryl phosphites has been studied only with diphenyl phosphite, which is almost quantitatively transesterified by butyl, isopentyl, hexyl, octyl, nonyl, and decyl alcohols even at 100° without the phenol being distilled off from the reaction mixture during the process[111,112]. The duration of the reaction depends on the molecular weight of the alcohol used, normally varying over the range 4–10 h. The synthesis goes smoothly both in the presence and in the absence of a catalyst (sodium). Yields of the products of complete transesterification are 90–95%. It is noteworthy, however, that our own experiments under the conditions described have not given positive results.

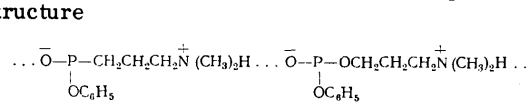
Diphenyl phosphite reacts readily with substituted alcohols[111]. The reactions with 2-chloroethanol and ethyl glycollate, for example, gave the complete transesterification products in yields of 93% and 94% respectively.

Diphenyl phosphite is also readily transesterified by aminoalcohols. When equimolecular quantities of diphenyl phosphite and dimethylaminoethanol are mixed, for example, heat is evolved, and one mole of phenol separates; the crystalline product is formed in almost quantitative yield. The substance is soluble in water and is readily oxidised. In view of this, and also the results of elementary analysis, the compound may be assumed to be an internal salt of dimethylaminoethyl phenyl hydrogen phosphite:

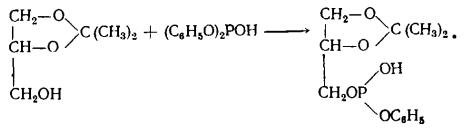


Diethylhydroxyethylmethylammonium iodide reacts with greater difficulty.

Alcoholysis of diphenyl phosphite with dimethylaminopropanol under similar conditions yields a thick oil, which does not crystallise on prolonged standing. The product is soluble in certain polar organic solvents, e.g. in *p*-cresol. Its molecular weight (determined cryoscopically in this solvent) is 4000. The structure of the polymer was not elucidated. By analogy with the product of the transesterification of diphenyl phosphite with dimethylaminoethanol, we may assume that in this case the polymer has the structure

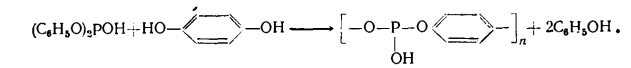


Alcoholysis of diphenyl phosphite with isopropylidene derivatives of glycerol and metriol gives good yields of the isopropylidenedioxyalkyl phenyl hydrogen phosphites[80]:



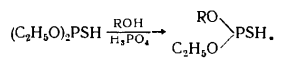
Cross-linked polyphosphites have been obtained by the transesterification of diphenyl phosphite with α-methyl-, *N*-phenyl-, and α-propyl-glucosides[113].

Reaction of diphenyl phosphite with quinol yields a poly(arylene phosphite)[62]:



The poly(arylene hydrogen phosphite) is unstable to hydrolysis whether in neutral, acid, or alkaline medium.

Diethyl phosphorothioite is transesterified by alcohols with considerably greater difficulty than are dialkyl (or diaryl) phosphites: in this case only 32–39% yields of the partial substitution products are obtained[114]:



IV. TRANSESTERIFICATION OF PHOSPHONITES

Few papers have been published on the transesterification of normal esters of alkylphosphonous acids. The complete transesterification of diethyl butylphosphonite with butanol in the presence of metallic sodium occurs more readily than in the case of phosphites[115]. Transesterification of simple phosphonites with substituted alcohols containing electrophilic groups takes place under more severe conditions[88], the yields of the complete transesterification products being considerably diminished. Thus diethyl phenylphosphonite is transesterified by ethyl glycollate, tetrahydrofurfuryl alcohol, and furfuryl alcohol in the presence of sodium to give yields of 40.7%, 61.5%, and 19.2% respectively. In the absence of catalysts the alcoholysis of phosphonites results in the formation of mixtures of complete and partial transesterification products[58,116]. Unsymmetrical phosphonites, obtained by the transesterification of phosphonous esters with 2-alkylthioethanols, have been used for the synthesis of Systoxes[58,117].

The polytransesterification of dimethyl and diethyl phenylphosphonites and diethyl ethylphosphonite with equimolecular quantities of various glycols has been investigated[118]. The rate and the degree of completion of the reaction decrease in the sequence ethylene, diethylene, and tetraethylene glycols. The reaction was found to involve the intermediate formation of cyclic phosphonous esters.

The transesterification of diethyl phenylphosphonite with glycerol and pentaerythritol has been studied[107] with various relative proportions of the reactants and under various temperature conditions. The best results were obtained at 140°. The polymers obtained were thick, viscous liquids or vitreous masses, yellow or light brown in colour, insoluble in water but soluble in benzene and dichloroethane; many of the polyesters were soluble in

ethanol and dimethylformamide. Bis-2-chloroethyl phenylphosphonite shows a great tendency to transesterification [119], undergoing the reaction even at 30–40°.

Phenyl esters of alkyl(or aryl)phosphonous acids react readily [72]:

$$RP(OC_6H_5)_2 \xrightarrow{R'OH} RP(OR')_2,$$

the yields of the complete transesterification products being 78–84%. Diphenyl methyl- and phenyl-phosphonites have been successfully employed for the phosphorylation of various nucleotides [120] and glucosides [113], mixed esters being obtained in the first case, and network polyphosphonites in the second case.

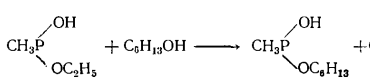
The transesterification of aromatic esters of phosphonous acids with dihydric and trihydric phenols yields poly(arylene phosphonites) [82]:

$$RP(OC_6H_5)_2 + HOR'OH \xrightarrow{-C_6H_5OH} \left[-\underset{\displaystyle R}{\overset{|}{P}}-OR'O-\right]_n,$$

where R = CH_3, C_6H_5 and R′ = C_6H_4, $C_6H_4.C_6H_4$, $C_6H_4.C(CH_3)_2.C_6H_4$. Diphenyl methyl- and phenyl-phosphonites have been used as the phosphorus-containing components, and quinol, biphenyl-*pp*′-diol, and 2,2-diphenylpropane-*pp*′-diol as the phenolic components. Phenolysis was accomplished quite readily, and was accompanied by the separation of almost the theoretical quantity of phenol. The yields of polyphosphonites were close to quantitative.

Hardly any work has been done on the transesterification of dialkylphosphinous esters. There is only the statement that the alcoholysis of propyl dipropylphosphinite with β-hydroxypropionitrile, 2-hydroxyethanol, and furfuryl alcohol in the presence of sodium gives the complete transesterification products in yields of 44.3%, 28.4%, and 36.3% respectively [88].

A detailed study has been made of the transesterification of acid esters of methylphosphonous acid. The dependence of the reaction on the temperature conditions, the relative proportions of the reactants, and the catalyst has been investigated with the interaction of ethyl hydrogen methylphosphonite and hexan-1-ol as example [121]:



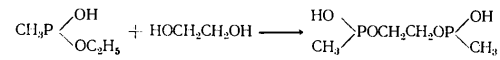
The best results are obtained with equimolecular proportions of the reactants in the presence of metallic sodium as catalyst at 150–160°. The temperature can be somewhat lower if the process is conducted in a slight vacuum, but the yield of phosphonite is then diminished. A definite though smaller catalytic effect is also shown by zinc borate; zinc chloride, orthophosphoric acid, and aluminium chloride impede transesterification.

The transesterification of phosphonites takes place more readily the lower the molecular weight of the alkoxy-residue. Under optimum conditions (after 5 h) the yields obtained with hexan-1-ol were respectively 71.5% and 44.4% for methyl and isopropyl methylphosphonites. Methyl methylphosphonite (yield 64.3%) constitutes an exception to this rule, for it partly decomposes under the reaction conditions.

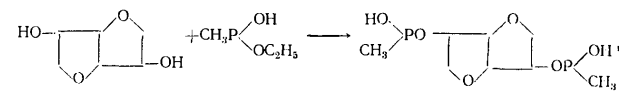
Transesterification occurs more readily with primary alcohols, and less readily with secondary alcohols [121]. Attempts to effect alcoholysis with tertiary alcohols (in the case of 1,1-dimethylpentan-1-ol) were unsuccessful.

Investigation of the transesterification of ethyl hydrogen methylphosphonite with alcohols containing functional groups has shown that the yield of ester depends substantially on the nature of the substituent and on its position in the alcohol molecule: the more electrophilic the substituent and the closer it is to the carbon atom attached to the hydroxyl the more difficult is it to effect transesterification [88]. Thus 2-chloroethanol reacts with greater difficulty (yield 45%) than does 3-chloropropanol (60%), furfuryl alcohol (10%) reacts less readily than does tetrahydrofurfuryl alcohol (69.7%), etc. Ethyl hydrogen methylphosphonite readily undergoes alcoholysis with 2-methoxyethanol and aminoethanol, the yields of the transesterification products being 70% and 100% respectively.

Ethyl hydrogen methylphosphonite reacts smoothly with glycols to give good yields of bismethylphosphonites [122], e.g.



A similar reaction occurs with 1,4:3,6-dianhydromannitol:



as also with 1,2:3,4-di-isopropylidenegalactose [123]. Transesterification of ethyl hydrogen methylphosphonite with 1,4:3,6-dianhydrosorbitol occurs under more severe conditions, and yields only the monophosphonite of dianhydrosorbitol. When isopropylidene derivatives of glycerol and metriol are used in this reaction, the isopropylidenedioxyalkyl phosphonites are formed in high yields [80].

It has not proved possible to transesterify an acid ester of methylphosphonous acid with ethylene glycol to involve only one of the hydroxyls: in all cases, even with a large excess of the glycol present, only the bisphosphonite is formed [122].

The bisphosphonites obtained are thick liquids or else solids, which can be distilled without decomposition only in a high vacuum. They are sparingly soluble in most of the usual solvents; the simplest of them are soluble in water and in alcohol [124].

A phosphorylated cellulose having a high phosphorus content (up to 19.1%) has been obtained by transesterifying methyl and ethyl hydrogen methylphosphonites with cellulose, while a phosphorylated polysaccharide containing up to 23% of phosphorus has been obtained with inulin [81].

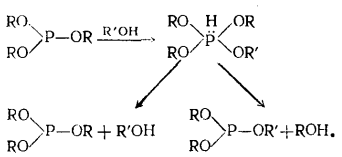
Diethyl methylphosphonodithioite reacts with both primary and secondary alcohols to form methylphosphonous esters [125]:

$$CH_3P(SC_2H_5)_2 + 2ROH \longrightarrow CH_3P(OR)_2 + 2C_2H_5SH.$$

The yield of phosphonites did not exceed 25–50%, being lower than in the transesterification of acid phosphonous esters. The probable reason is that the thiol liberated in the reaction and its oxidation product (disulphide) interact with the phosphonite to form a complicated mixture of compounds.

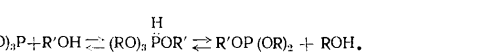
V. MECHAMISM OF THE TRANSESTERIFICATION OF ESTERS OF ACIDS FORMED BY TERVALENT PHOSPHORUS

No detailed study has been made of the mechanism by which esters of acids containing tervalent phosphorus are transesterified. The mechanism is assumed[55,121] to involve alternating addition of a proton to the phosphorus atom with addition of an alkoxide anion to the phosphonium cation and elimination of alcohol from the intermediate product containing quinquevalent phosphorus to form either the original or a different phosphite or phosphonite:



Indirect evidence for the formation of an intermediate addition product is provided by data on the mechanism of the Arbuzov reaction and its various modifications, and also by experimental results on the alcoholysis of esters of tervalent phosphorus acids.

The primary step in the reaction is necessary but insufficient to achieve transesterification of the phosphite (or phosphonite). As shown above, the adduct can break down in two ways. An equilibrium is established in the alcoholysis of any phosphite with any alcohol:



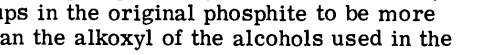
Transesterification will take place if the equilibrium is displaced to the right, i.e. if an alkoxyl (or phenol residue) of the original phosphite — not the alkoxyl of the alcohol taken for the transesterification — splits off from the adduct. Thus the second step in the reaction — cleavage of the addition product — plays the decisive part in the process of transesterification, and probably determines not only the direction but also the rate of the reaction.

Which alcohol will be eliminated from the intermediate product depends directly on the electrophilic character of the alkoxy(or phenoxy)-groups involved. It is obvious that the more electrophilic an alkoxyl the more preferentially will it be eliminated together with a proton in the form of the "more acidic" alcohol. Hence it is desirable, in the preparation of phosphites by transesterification, for the alkoxy-groups in the original phosphite to be more electrophilic than the alkoxyl of the alcohols used in the reaction.

The above arguments are consistent with data obtained for the transesterification of diethyl, bis-2-chloroethyl, bis-2-fluoroethyl, and diphenyl phosphites with decanol, of diethyl phosphite with β-hydroxypropionitrile, 2-chloroethanol, and 2-methoxyethanol, of ethyl hydrogen methylphosphonite with aminoethanol, 2-methoxyethanol, β-hydroxypropionitrile, 3-chloropropanol, etc.

The transesterification equilibrium can be shifted to the right by distilling off the alcohol which is liberated. This procedure is widely used to prepare various phosphites when the liberated alcohol boils at a lower temperature than the original alcohol.

Another possible mechanism consists in attack on the oxygen atom by an alkyl cation (formed by heterolytic cleavage of the alcohol) with simultaneous liberation of the alkyl cation of the original ester[55]:



However, this reaction is only of secondary importance, since transesterification with the two optically active butan-2-ols and with optically active neopentanol yields phosphites which on hydrolysis give alcohols having 75% and 100% respectively of the original optical activity. If only the second type of reaction had taken place, hydrolysis of the products of transesterification should have produced optically inactive alcohols.

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NEW THEORIES OF THE CHEMICAL NATURE OF LUMINESCENCE CENTRES IN ZINC SULPHIDE PHOSPHORS

A.M. Gurvich

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I. INTRODUCTION

The chemistry of sulphide phosphors of the ZnS type is an important and very interesting area of solid state chemistry†. Because of their high luminescence efficiency under a variety of excitation conditions, and of the unusually wide range of their properties, crystal phosphors of this class have found extensive technical applications in television tubes, radar screens, oscilloscopes, electron--optical converters, X-ray screens, electroluminescent panels, electron microscopes, dosimeters and detectors of different types of radiation, etc. Cadmium sulphide crystals, which belong to the same class of materials, are among the most sensitive photoconductors.

The influence of very small traces of impurities on these two properties of crystalline sulphides — luminescence and photoconductivity — was recognised at the turn of the century. The efficiency with which the absorbed radiant energy is transformed into visible light (of spectral composition determined by the nature of an impurity, termed the activator) suggested that energy transfer takes place from the sites where energy is absorbed to the sites where the activator is located. This gave rise to the theory that the luminescence centres are special groupings where the act of light emission occurs. The ability of ZnS and CdS crystals to transmit the absorbed energy with high efficiency to the luminescence centres accounts for their high luminescence yield, their high photoconductivity, and the extreme sensitivity of phosphors of this class to a number of impurities, which can effect the optical properties of these phosphors even at a concentration of 10^{-6}–10^{-8} gramme per gramme of the sulphide.

Elucidation of the nature of the luminescence centres and of the relationship between the optical properties of phosphors and the structure of these centres, being one aspect of the more general problem of establishing the relation between the atomic-molecular structure and the properties of materials, is the key problem in luminescence and is of great importance in the general development of solid state chemistry and physics. Yet the first serious studies in this field began only towards the end of the 1940's, when research on the kinetics of luminescence and on the accompanying internal photoeffect provided, on the basis of the band model of solids, a fairly orderly picture of the physical effects involves in the luminescence of zinc sulphide luminous compositions. The work done in the last 15–20 years and still in progress has significantly changed our ideas on the nature of the luminescence centres and on the processes by which they are formed, and has made it clear that the solution of the problem lies in the domain of chemistry to a much greater extent than had originally been realised. Many difficulties still remain to be overcome, in particular those associated with the extreme sensitivity of the optical properties of zinc sulphide phosphors to various impurities present at a concentration level which defies analytical control with the required degree of precision, and also with our inadequate knowledge of the nature of structural defects and of the role played by these defects in the formation of sulphide phosphors. The situation is made worse by the abundant literature and by the close interplay of chemistry and physics: as a result, authors attempting to interpret their

† Luminescent crystals of zinc sulphide were prepared for the first time 100 years ago by Sidot, in Sainte-Clare Deville's laboratory.

results are often unaware of many relevant factors discussed in earlier publications. This causes a great deal of confusion and inconsistency in many of the papers devoted to the present problem. Hence, a review article discussing the work of all the main research schools and all the most important points of view would be very timely: such is the aim of the present paper, with the stipulation that we shall not attempt to consider all the questions which have a bearing on our problem. The reason for this is that zinc sulphide phosphors contain centres of two types. One type of centres, for example those produced by manganese or rare-earth ions, gives rise to luminescence as a result of electronic transitions within the activator ion itself ("direct activation"). The radiation from centres of the second type is not characteristic of the particular activator to the same extent. Thus, ZnS phosphors activated by impurities as diverse as Ag, Cu, Al, and Cl, can, under certain preparative conditions, produce blue radiation of very similar spectral composition. In this case we cannot ascribe the observed luminescence to electronic transitions within the ions (or atoms) of the activator. Centres of this second type are the most characteristic of zinc sulphide phosphors, the most important from a practical point of view, the most thoroughly investigated, and the least understood. The present paper is devoted to a discussion of centres of this type.

II. ACTIVATORS AND COACTIVATORS

1. Luminescence Centres Produced by Activators

Luminescence centres were originally thought to be rather coarse aggregates of many atoms, but in the early 1930's the suggestion was put forward, on the basis of several results, that the centres consist of single atoms (or ions) of the activator located at lattice or interstitial sites[1-4]. It has been commonly assumed, with Lennard[5], that only heavy metal atoms can act as activators. Since their energy levels are closely spaced[6], they emit radiation which is not absorbed by the phosphor matrix. The discovery[7] that zinc sulphide can emit bright blue luminescence in the absence of any deliberately added activators had a marked effect on the development of views on luminescence centres. This discovery was made possible by the improved methods of preparation of sulphide of a high degree of purity. An analogous phenomenon was observed with zinc oxide. Since it was assumed that only metals can serve as activators, the effect was interpreted as self-activation by the excess of zinc produced by thermal dissociation of the zinc oxide and sulphide[8], experimental confirmation being forthcoming in the case of ZnO. Arguing that ZnS should behave very much like ZnO, Seitz[2,9] suggested that free atoms of Zn give rise to luminescence centres by moving to interstitial sites, and that activation by silver and copper occurs by a similar mechanism. In favour of this point of view, Riehl and Ortmann[10] put forward some arguments based on earlier experiments by Tiede and Weiss[11], who had shown that, when a mixture of roasted ZnS and copper sulphide is heated, the diffusion of Cu, leading to the formation of luminescence centres, begins at a temperature as low as 330°. Adopting an ionic model for zinc sulphide, we can think of the material as an array of close-packed sulphur ions with half of the tetrahedral cavities occupied by zinc ions[12]. The presence of free tetrahedral cavities accounts, according to Riehl and Ortmann, for the diffusion of the activator deep into the lattice even at relatively low temperatures, the process being assisted by the fact that the activator enters the lattice in the form of atoms rather than ions. However, Riehl and Ortmann subsequently rejected[13] the last assumption. Bundel'[14] produced additional arguments in favour of the Schleede–Seitz–Riehl hypothesis. According to his observations, the quenching of luminescence produced by heating the phosphor in sulphur vapour occurs more readily the lower the dissociation pressure of the sulphide of the activator metal. This may be due to the fact that activation occurs when activator atoms formed by thermal decomposition of their sulphides are introduced into the crystal lattice[15]. Bundel' quotes as further evidence for this point of view the fact that luminescence quenching by vacuum heat-treatment occurs more readily in "self-activated" phosphors than in phosphors activated by copper or silver, in keeping with the greater volatility of Zn and Cd as compared with Ag and Cu[16]. Very similar views were put forward by Cherepnev[17-20], who considered that the activator may be present in zinc sulphide in a state involving different degrees of dispersion.

The model according to which luminescence centres are formed by free atoms of the activator was dominant until the end of the 1940's. However, several authors have doubted the correctness of the suggested "self-activation" of zinc sulphide by zinc in excess of stoichiometry when the material has been heat-treated in the presence of a flux and oxygen[21], and also the possibility that copper can exist in an atomic state in zinc sulphide[22] and that ZnS–Ag luminescence centres are created by atomic silver. (The latter assumption is inconsistent with the deleterious effect of a reducing atmosphere on ZnS–Ag[23].) A fundamental defect of the above model, stressed by a number of workers[21,24,25], is that it fails to explain a very remarkable feature of zinc sulphide phosphors — the favourable effect of halides, commonly used as fluxes, on their formation — which was noted long ago in the literature[5,26]. Whereas the flux used in the preparation of other phosphors serves only to lower the temperature to which the charge has to be heated, and often is not merely unnecessary but may even diminish the brightness of the luminescence[24], in the case of sulphides the use of halide fluxes (usually alkali or alkaline-earth metal chlorides) is essential to the achievement of efficient luminescence. Schlegel[27] pointed out that considerable quantities of $ZnCl_2$ are formed when ZnS is heated with NaCl, and, whilst ascribing this to reaction between the ZnS and NaCl, he nevertheless suggested that the role of the flux is to assist dissociation of the sulphide of the activator metal. Gugel'[28] stressed the importance of exchange reactions between ZnS and the chlorides of alkali and alkaline-earth metals, and suggested that these reactions assist diffusion of the activator into the crystal lattice of the sulphide by eroding the surface. The direct participation of chlorine in the formation of luminescence centres has also been considered[24,29]. An important function of the chloride, unrelated to its mineralising action, was convincingly demonstrated by Strange[24], who heated ZnS in evacuated quartz bulbs at 1000° for several hours, and found that the characteristic green luminescence of ZnS–Cu appeared in the presence of 0.001% CuS and an equivalent amount of NH_4Cl, but that the luminescence was weak or altogether absent in the presence of CuS alone (i.e. without NH_4Cl) or when the ZnS was heated without any intentional additive. A similar result was obtained with silver.

The role of halides in the formation of phosphors was examined in detail in a series of papers by Kröger[30-33], which marked the beginning of a new stage in the study of the nature of luminescence centres. Whereas the first stage of these researches, discussed above, was made possible by the development of effective methods for the purification of zinc sulphide from metallic activators, especially Cu, and luminescence "quenchers", such as Fe, Ni, Co, which led to the discovery of "self-activated" ZnS phosphors, the second stage began when attention was turned to the need to remove anionic impurities as well from the experimental material. In order to remove the chloride and oxygen present in commerial "phosphorescent grade" ZnS, Kröger subjected the material to a preliminary heat-treatment in a stream of H_2 or H_2S. Later workers[34-37] recommend deoxidation and dechlorination of ZnS by a two-stage treatment in hydrogen sulphide, first at a relatively low temperature (400°), and then at a more elevated temperature (900–1200°), because if the process is carried out with a high initial temperature the recrystallisation which occurs at the same time inhibits the removal of impurities from deep within the crystals. Another experimentally valuable innovation introduced by Kröger was to replace heating with a flux by heating in an atmosphere of HCl and H_2S. This permitted a more precise regulation of the preparation process and made it easier to interpret the results. The method has since found technical applications, particularly in the synthesis of electroluminescent materials[38,39].

Kröger showed, in agreement with the results of Strange[24], that ZnS–Cu, ZnS–Ag, and ZnS s/a ("self-activated") phosphors are not formed in an atmosphere of H_2S when the system is free from chlorine. The normal luminescence appears on heating in a stream of gas containing HCl. The refinements in experimental technique mentioned above allowed these phenomena to be observed with satisfactory reproducibility. Kröger interpreted his results on the basis of the principle of charge compensation, well known from crystal chemistry and mineralogy[40,41] and successfully applied to the chemistry of semiconductors[42]. Essentially, this principle states that in the formation of substitutional solid solutions the sum of the charges on the substituent ions must be equal to the sum of the charges on the ions replaced. This principle is a simple corollary of the requirement that the electrical neutrality of the crystal must be preserved. If, for example, a Zn^{2+} ion is replaced by a Cu^{+} ion, the result is to create a defect with an effective charge of -1, which we propose to denote Cu'_{Zn}. This charge can be compensated by the simultaneous insertion of a Cl^- ion in an S^{2-} site, which produces a defect with an effective charge of +1 ($Cl^{\cdot}_{S}$). In the absence of chlorine, compensation can be achieved by the formation of an anion (sulphur) vacancy of effective charge +2 ($V^{\cdot\cdot}_{S}$) and therefore able to balance the charges of two Cu′ defects; however, Kröger regards the formation of solid solutions in which the compensation is of this type as thermodynamically the less probable. In the terminology of crystal chemistry[41], the formation of normal isomorphous mixed crystals ZnS.CuCl with heterovalent replacement (mixed crystals of a new kind, in Grimm's terminology) proceeds more readily than the formation of anomalous mixed crystals $ZnS.Cu_2S$ with addition or subtraction. ZnS and CuCl have the same atomic ratios of constituent elements and therefore have chemical formulae of the same type, similar atomic dimensions, and a similar bond type[43]. Hence, the two compounds are isomorphous, and are quite likely to form mixed crystals. This is confirmed by the fact that the concentrations of Cl and of Cu in the ZnS lattice increase in the same proportion[32,44,45]. Under these conditions the concentration of Cl can reach much higher values than when ZnS is heated in the presence of a copper-free chloride flux. An analogous situation exists in the case of silver activation. Formation of AgCl has been shown, by chemical analysis[46], to take place when sulphide phosphors are heated with silver and a chloride flux under normal conditions (in the air). It may also be imagined that charge compensation occurs by the simultaneous introduction of sulphide activator and zinc chloride[47]:

$$n\mathrm{ZnS} + \mathrm{Cu_2S} + \mathrm{ZnCl_2} \rightarrow \mathrm{Zn}_{n+1}\mathrm{Cu_2S}_{n+1}\mathrm{Cl_2}. \qquad (1)$$

The zinc chloride can be replaced by the sulphide of a tervalent metal[48], such as Al_2S_3:

$$n\mathrm{ZnS} + \mathrm{Cu_2S} + \mathrm{Al_2S_3} \rightarrow \mathrm{Zn}_n\mathrm{Cu_2Al_2S}_{n+4}. \qquad (2)$$

In this case charge compensation occurs through the formation of $Al^{\cdot}_{Zn}$ defects in equivalent amounts of Cu'_{Zn}. The activator and the tervalent metal are sometimes added to the charge in the form of a double sulphide, $CuAlS_2$, $CuInS_2$, $AgGaS_2$, etc.[49,50] The favourable effect of some tervalent metals on the formation of ZnS phosphors was recognised even before the work of Kröger[51], but application of the theory of charge compensation has made it possible to give a unified explanation of the effect of chloride and of tervalent metals, and furthermore has led to the development of a much wider range of luminescent systems of this type. The action of tervalent metals can be taken as proof[52] that Cu and Ag enter lattice sites, i.e. form substitutional solid solutions, in ZnS, since the effect could not occur if interstitial solid solutions were formed. From the fact that the spectral composition of the radiation from ZnS–Cu and ZnS–Ag phosphors is independent of the type of compensating ion it was concluded[33] that the activator and the compensating ion are located far from each other in the lattice, and that the luminescence centre does not contain the latter ion. Since halogens and tervalent metals merely assist penetration of the activator into the phosphor matrix but do not affect the luminescence spectrum, these substances have been termed "coactivators". We can see from the Periodic Table that activators, which include Au[53] and also P, Sb, and As[54-56] besides Cu and Ag, occupy a position to the left of the constituent elements of the phosphor in the neighbouring group, whereas the coactivators are found to the right of the main components[57] (Fig. 1). Under certain conditions, however, activators and coactivators can exchange roles[58,59].

As a rule, halides are more effective coactivators than are tervalent metal sulphides, in particular because the latter (especially Al_2S_3) are readily hydrolysed and oxidised.

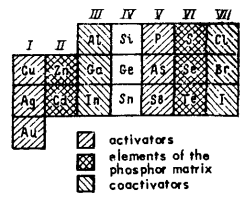

Fig. 1. Position of activators and coactivators of binary compounds of the ZnS type in the Periodic Table[57].

Indium dissolves in ZnS more easily than other Group III metals[60], and chemical analysis has shown[61] that this metal can enter the lattice. It has also been reported[60] that a higher concentration of Cu can be introduced into ZnS in the presence of In. Aluminium, on the other hand, goes into the ZnS lattice with difficulty in the absence of an activator[59]. Since aluminium salts are easily converted into Al_2O_3, which is transformed into the sulphide only to an insignificant extent[62] when heated in H_2S, the preparation of ZnS–Cu,Al and ZnS–Ag,Al requires special precautions[61] to enable a large proportion of the added Al to enter the lattice. The presence of the activator favours the dissolution of Al_2S_3, and therefore also makes possible its formation. In any case, the ability of aluminium to act as a coactivator has been demonstrated on many occasions[35,36,48,50,61,63]. Experiments in which Al is added to the charge in the formation of Al_2O_3 without an activator[64] give no grounds for refuting this statement. It is equally incorrect to ignore, as is often done, the fate of the partner of the impurity ion which replaces an ion of the main lattice, since we are dealing with the formation of a solid solution of the impurity compound, not of the free element.

When applying the principle of charge compensation, we have assumed that ZnS is an ionic crystal. In fact, however, the bond in zinc sulphide is more covalent than ionic[43,65,66]. But this does not alter the situation, since the principle of charge compensation can be replaced by the more general principle of valency compensation[67]. Consider the covalent model of a ZnS phosphor. The zinc atom has two valency electrons occupying a single s-shell ($4s^2$), and the sulphur atom has six valency electrons ($3s^2p^4$). In the crystal lattice every zinc atom is surrounded by four sulphur atoms, and every sulphur atom by four zinc atoms. The valency electrons are shared, as it were, between the zinc and the sulphur. As a result, four hybrid sp^3 orbitals appear in each atom[68], and form tetrahedral bonds where they overlap similar orbitals of neighbouring atoms. If an impurity atom is added to such a crystal, it tends to take up the electronic structure of the Zn and S atoms of which the host lattice is composed. If, for example, a sulphur atom with six valency electrons is replaced by a Cl atom, having seven valency electrons, one "excess" electron appears; this is very easily lost by the Cl atom, and enters the conduction band. The introduction of a Cu atom with one valency electron at the site of a Zn atom leads to the formation of a defect which, in contrast, tends to capture the one electron which it lacks. It is obvious that impurities of the Cl type will raise the electronic conductivity: in the study of semiconductors these impurities are called donors. Impurities similar to Cu decrease electron conduction or increase hole conduction: these are called acceptors. When both donors and acceptors are present together in the crystal, electrons tend to pass from the former to the latter. This process is accompanied by a gain in energy. As a result, the solubility of an acceptor impurity is increased by the simultaneous dissolution of a donor impurity. It is interesting to note that this phenomenon occurs also in elementary semiconductors. For example, the solubility of lithium in silicon is increased by the presence of boron[69]. Equal numbers of donors and acceptors produce what is known as a compensated semiconductor. The most effective ZnS–Ag,Cl and ZnS–Cu,Cl phosphors also appear to be compensated semiconductors[70]. If the number of acceptors is not equal to the number of donors, compensation can arise through sulphur vacancies in the case of an excess of acceptors, or through zinc vacancies in the case of an excess of donors[71,72]. However, after loss (or gain) of one electron the vacancy acquires a charge, which makes the loss (or gain) of a second electron more difficult. This is, obviously, one of the reasons why AgCl and CuCl dissolve in ZnS more readily than do Ag_2S and Cu_2S. The higher solubility is also partly due to the fact that the energy expenditure associated with the formation of vacancies is eliminated[47].

Studies of the influence of impurities on the dark conductivity and on the photoconductivity of zinc and cadmium sulphides have confirmed that activators (Ag and Cu) act as acceptors when they are introduced into the lattice, whereas coactivators (Cl, Ga, In, etc.) are donors[61,65,73–76]. This is one of the weightiest arguments[75] against the hypothesis that Ag and Cu enter the lattice as free atoms, since if that were the case they would give rise to donor defects[77]. It has been shown that ZnS, CdS, and (Zn,Cd)S phosphors are n-type semiconductors (i.e. their conductivity is due to electrons)[78,79], the conductivity increasing when cadmium and zinc chlorides are introduced into the lattice[73,76]. Activation with silver and copper does not convert the n-type conduction into p-type (positive-hole) conduction because of the high ionisation energy of the acceptor defects produced in the lattice of the sulphides[65], but there is a decrease in the n-type conduction, and this can be taken as evidence that Ag and Cu act as acceptors. Hence it is incorrect to assume, as is sometimes done[80,81], that the n-type conduction points to activation of ZnS by the free metals.

The hypothesis of activation by free metals is also inconsistent with experiments on the electrolytic activation of zinc sulphide with copper[63,82] and with the results of a study of the magnetic properties of ZnS phosphors. Measurements of the temperature variation of the magnetic susceptibility of ZnS–Cu phosphors[71] by a method sensitive to 0.0001% of a paramagnetic impurity have shown that copper enters the lattice in a diamagnetic state. This argues not only against the hypothesis of activation by free copper atoms, which have one unpaired s-electron, but also against an earlier suggestion[25] that the "green" copper centres are formed by a Cu^{2+} ion. We should also remember that CuS is unstable above 200°.

As we mentioned above, the fact that the nature of the coactivator does not affect the spectral positions of the green band of ZnS–Cu and the blue band of ZnS–Ag phosphors has been interpreted as a consequence of the spatial separation of activator and coactivator. This means that the phosphor contains, as a rule, at least two kinds of defects, which are not related to one another. On an energy diagram (or band diagram) these defects are represented by two kinds of level in the forbidden gap: levels close to the conduction band, formed by the coactivator, and levels located above the valency band, formed by the activator (Fig. 2*a*). It follows from the above arguments that in an unexcited phosphor, which is a compensated semiconductor, the electrons reside mostly on the activator levels, whose distance from the conduction band determines to a first approximation the luminescence spectrum. On excitation the electrons pass into the conduction band, and may be captured by the coactivator levels, from which they are freed by thermal vibrations. Different coactivators can be expected to give rise to levels (electron traps) at different depths below the conduction band. The application of the so-called thermal glow method, which enables trap depths to be measured, has demonstrated the correctness of this hypothesis: it was found that the depth

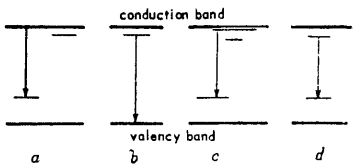

Fig.2. Energy-level models of the centres (explained in the text). The arrows denote electronic transitions.

of the electron traps is indeed determined by the nature of the coactivator and is independent of the nature of the activator[83-85]. In this way, Blokhintsev's hypothesis[86] of the spatial separation of luminescence centres and traps was verified, and furthermore the nature of the defects which may be responsible for the appearance of the trapping levels was established. The fact that the depth of the latter is independent of the activator does not in any way imply that the thermoluminescence and the afterglow are also independent of the activator, for the activator takes an active part in the luminescence process. Thus, in the case of a phosphor with two activators the thermal glow curves for the bands corresponding to these activators are not identical, since as the temperature is raised the probability of electron emission from the valency band to the activator levels increases, producing shorter-wavelength radiation. Under these conditions, holes migrate to the luminescence centres formed by the second activator, and are captured by them. Hence, the contribution of the long-wavelength band to the thermoluminescence spectrum increases with increase in temperature. The dependence of the afterglow on the nature of the activator can be explained in a similar way. It is also clear that the intensity of the thermoluminescence is related not only to the concentration of the trapping centres but also to that of the luminescence centres, since the radiation intensity I is proportional to the product of the concentration n of electrons freed from the traps and the concentration p_t of holes localised at luminescence centres: $I = \beta n p_t$, where β is the coefficient of recombination. Neglect of these principles leads to groundless conclusions[87,88] as to the relation between electron traps and luminescence centres.

Thus, we can now point to a whole series of proofs that chlorine and other coactivators actually enter the sulphide lattice at the same time as the activators. The fact that a coactivator must be present for activation by copper or silver to occur, established by the work of Strange, Kröger, and Schleede[89], was later confirmed in experiments with evaporated films[90] and single crystals[76]. It should be noted that the majority of workers (including the originators — Schleede[89,91] and Riehl and Ortmann[13] — of the hypothesis that the sulphides are activated by free atoms) now believe that the blue silver band and the green copper band are due to Ag^+ and Cu^+ ions located at lattice sites. (When referring to ions, here and subsequently, we have in mind the fact that the activators enter the lattice as compounds rather than as free atoms.) We must point out, however, that the mere fact that an impurity such as Cl must be present to cause luminescence to appear in the band of any particular activator cannot be taken as proof that this impurity is a coactivator, since cases are known in which the role of the impurity is to sensitise the luminescence[92-94], i.e. to form centres which absorb the energy of the exciting radiation and later transfer it to the activator centres.

2. Association of Activators and Coactivators

It has been suggested[30,95] that, at the normal temperature of formation of ZnS phosphors (800–1200°), the coulombic interaction of the activator and coactivator ions will favour their association, whereas the tendency of the system to maximise its entropy will act in the opposite sense. According to Prener and Williams[57,72,96], the relatively high impurity concentration (10^{-4} g-atom mole^{-1}) and the relatively low dielectric constant of ZnS should cause the tendency to association of the activator and coactivator to predominate, forming donor–acceptor pairs. These pairs of activator and coactivator atoms, associated as second or third nearest neighbours, are identified with the luminescence centres. Thus, Prener and Williams ascribe to the coactivator even more active a role than does Kröger, since they assume that it forms part of the luminescence centre by contributing an excited level close to the conduction band (Fig. 2*c*). This must increase the probability of capture of a conduction electron by the luminescence centre[57,97]. The suggestion that the luminescence centre of ZnS–Cu phosphors includes an excited level close to the conduction band is supported by the observation[98] that at low enough temperatures the photoconductivity of ZnS–Cu single crystals irradiated with light corresponding to the characteristic absorption band of the Cu centres vanishes, whereas the luminescence persists. However, the excited level is not necessarily associated with the presence of a coactivator. Prener and Williams quote[72] as an experimental proof of their theory the fact that the luminescence of ZnS is unaffected by the transmutation of ^{65}Zn atoms (obtained from ^{64}Zn by irradiating the sample with a neutron flux) to ^{65}Cu atoms, despite the fact that in this case the Cu appears at lattice sites and the lattice contains randomly distributed Cl ions. However, this could be ascribed, rather than to absence of associated Cu–Cl pairs, to the fact that luminescence centres are formed by univalent copper, whereas the nuclear reaction yields bivalent copper at the lattice sites[99]. Thus, the Prener–Williams hypothesis can hardly be said to be substantiated for systems such as ZnS–Cu,Cl and ZnS–Ag,Cl, whose radiation has a spectral composition independent of the nature of the coactivator[48,61,90]. It is true that Williams[100] explains this by postulating electronic transitions from the excited donor level — or even from the bottom of the conduction band — to the main acceptor level, and states (in contrast to his earlier hypothesis) that the activator and coactivator atoms are situated at an appreciable distance from each other — no nearer than seventh-nearest neighbours — in systems of this kind. But when modified in this way the views of Williams are hardly different from the generally accepted views. We should note that the postulated direct participation of the coactivator in the makeup of the green luminescence centres of ZnS–Cu phosphors and the blue luminescence centres of ZnS–Ag phosphors conflicts with reports in the literature that phosphors can be prepared without valency compensation by a coactivator[63,101] if the preparative conditions are such that Ag^+ and Cu^+ ions can reside at lattice sites.

Moreover, studies of ZnS phosphors containing Group III elements as coactivators have revealed luminescence bands which can in fact be ascribed to associated centres. Kröger had established that the luminescence spectrum of these phosphors sometimes exhibits long-wavelength bands in addition to the normal luminescence bands due to the activator[48]. Since these additional bands, which lie in the orange–red region of the spectrum, shift towards longer

wavelengths with increase in the depth of the electron trap formed by the coactivator, the suggestion was put forward[83] that these bands are due to the recombination of free holes with electrons trapped at coactivator centres (Fig. 2*b*). Thus, the latter act as luminescence centres as well as trapping centres. However, an experimental determination of the depth of the traps has shown that the radiation associated with this process should lie on the short-wavelength side (rather than on the long-wavelength side) of the luminescence bands due to silver and copper[84]. For this reason, Hoogenstraaten[84] proposed that an electron trapped at a coactivator centre recombines with a hole in a localised level above the valency band ("holding state") rather than in the valency band itself. The observed dependence of the spectral position of the long-wavelength band on the nature of the activator has led to the conclusion[49] that this level is bound to the activator and that the corresponding luminescence centre is therefore the result of association of the activator and the coactivator. This is confirmed by the fact that the proportion of long-wavelength radiation in the spectrum increases when the concentration of activator and coactivator (taken in equimolar amounts) is raised. Bands in the orange–red appear only when coactivators whose concentration in the ZnS phase can reach quite high values are used (e.g. Ga, In, Sc). Aluminium, which enters ZnS with difficulty, does not give this effect.

An attempt was made[49] to interpret the nature of centres responsible for the long-wavelength radiation in terms of the above-mentioned theory of Prener and Williams, developed on the basis of concepts[102] similar to those used in the theory of strong electrolytes. Assuming that in this case the radiative transition occurs from the ground level of the donor to the ground level of the acceptor (Fig. 2*d*), Apple and Williams calculated that the centre responsible for this radiation must consist of atoms of the activator and coactivator associated as fourth–sixth nearest neighbours[49,100], when overlapping of the ground state of the acceptor and the ground state of the donor sets in. With larger separations of the activator and coactivator atoms this overlapping does not occur, and the spectrum of the radiation shows only the normal activator band. However, the smaller the distance between the activator and the coactivator atom, the nearer their levels move towards the corresponding bands. Therefore, once the long-wavelength radiation appears, it can be expected to shift towards shorter wavelengths when the concentration of activator and coactivator is raised still further, and to disappear completely when the association becomes very close, owing to the fact that the ground levels of the donor and the acceptor have penetrated into their corresponding energy bands. van Gool[61] found that the long-wavelength band probably consists of several sub-bands, but that an increase in the concentration of activator and coactivator causes a shift towards longer rather than shorter wavelengths. Nevertheless, there can be no doubt as to the associated nature of the luminescence centre in this case. The location of the excited level within the forbidden gap is confirmed by the fact that the long-wavelength band has a lower thermal stability than the short-wavelength band, which would be impossible if the transition took place from the bottom of the conduction band. It should be noted that a long-wavelength emission with similar properties has been observed also in the absence of the main activator (Ag, Cu), for example when In [103,104] or Ga [105] impurities are added to ZnS. The luminescence centre responsible for this effect could also result from some kind of association — most probably that of Ga$^{\cdot}$ (or In$^{\cdot}$) with $V_{Zn}Ga'$ (or $V_{Zn}In'$). [105]

Thus, the hypothesis that a coactivator enters the lattice at the same time as the activator during the preparation of sulphide phosphors, and that this gives rise to a normal substitutional solid solution, provides an explanation of a large number of phenomena encountered in the preparation and in the study of ZnS phosphors. Nevertheless, a great deal still remains to be explained. This is because, in addition to the normal solid solutions with heterovalent substitution, which include the most effective and technically important cathodo-, röntgeno-, radio-, and photo-luminescent materials, solid solutions involving vacancies or interstices are also formed. A particularly difficult problem was that of interpreting the nature of the blue luminescence centre in self-activated (s/a) ZnS, and also the blue and the red luminescence of ZnS–Cu phosphors. Most objections to the views on the role of coactivators discussed above have been raised in connection with these particular problems. We shall consider these objections in the following sections.

III. LUMINESCENCE CENTRES OF "SELF-ACTIVATED" PHOSPHORS

In an attempt to produce a unified theory of the nature of the luminescence centres in s/a ZnS, ZnS–Ag, and ZnS–Cu phosphors, Kröger suggested[30] that the blue luminescence centre of s/a ZnS consists of a $Zn^{\cdot}$ ion whose deficiency of one positive charge is compensated by the simultaneous introduction of a Cl^{-} ion, so that in effect an s/a ZnS phosphor is a solid solution of the subchloride ZnCl in zinc sulphide. Generally speaking, subchlorides of this type are known. They are formed, for example, when the metal is dissolved in a melt of its normal chloride. Thus, Kröger's original hypothesis is equivalent to assuming that zinc in excess of stoichiometric (or, at least, partly reduced zinc) is involved in the formation of the luminescence centres. Subsequently, however, relying on the results of Bube[106–108], who had observed a blue luminescence in what he assumed to be pure ZnS which had been heated to a high enough temperature, and also noting that in the ionic model $Zn^{\cdot}$ is indistinguishable from a free electron in the conduction band, Kröger[109] changed his point of view and suggested that the blue luminescence centre in s/a ZnS is a cation vacancy (in this case, a zinc vacancy V'_{Zn}) with one electron missing from its immediate surroundings. Such a centre, however, should be paramagnetic, which conflicts with the results of magnetic susceptibility[71] and electron spin resonance (e.s.r.) measurements[110] on s/a ZnS phosphors. A model of the centre which satisfies these results was put forward by Prener and Williams[111], who suggested that the defect responsible for the formation of the centre is a zinc vacancy immediately adjacent to a donor impurity, e.g. $V_{Zn}Cl_S^{\cdot}$. This defect behaves very much like Ag'_{Zn} and Cu'_{Zn}. We should note that the association of a vacancy with an oppositely charged impurity defect is regarded as very important in the theory of the ionic conductivity of crystals[112].

Riehl and Ortmann's discovery[113] that no visible luminescence at room temperature is produced when ZnS is heated with NaCl in the complete absence of traces of oxygen revealed a new difficulty. This observation was confirmed by several other workers[36,76,114–116]. Similar statements on the role of oxygen are to be found also in earlier papers[117]. Although some authors[59,114] state that it is sufficient to introduce oxygen in combined form, e.g. as

ZnO, others[36,91,101,118] have been unable to obtain a blue luminescence when ZnO, moisture, and other oxygen compounds are present in the system. In this connection it is relevant to record a number of statements[113,115] that minute traces of free oxygen in the nitrogen or argon are sufficient to cause the characteristic blue luminescence when a ZnS(NaCl) charge is heated in a stream of these gases. Hence it is desirable to carry out these experiments under static conditions.

To explain these results it was initially suggested[114,118] that oxygen atoms are involved in the structure of the luminescence centres. However, this hypothesis conflicts with the fact that bright phosphors can be prepared from deoxygenated ZnS in HCl medium[30,115,119], and especially with the fact that a similar luminescence can be produced by introducing elements of Group III into the ZnS using an H_2S atmosphere[101]. In an attempt to make these two sets of data mutually compatible, and adopting the hypothesis that the luminescence centres are produced by V_{Zn} vacancies, Riehl and Sizmann[120] suggested that the Zn^{2+} ion tends to take up a position adjacent to the O^{2-} ion, which is smaller than the S^{2-} ion. In doing so, it can move into an interstitial site, i.e. into a normally empty tetrahedron, and this process gives rise to a V_{Zn} vacancy. However, this contradicts the above results (including those of Riehl and Ortmann[118]), according to which the presence of zinc oxide alone is insufficient to give rise to luminescence. Thus the situation concerning the nature of the luminescence centres in s/a ZnS was very confusing[121]. However, shortly afterwards, a way was found to correlate the results of Kröger[30,101] with those of Riehl and Ortmann: this was to make a combined study of the effect of preparative conditions on the luminescence and on the chemical reactions taking place in the system[46,67,91,122]. It was found that direct reaction between ZnS and NaCl with formation of $ZnCl_2$, whose possibility had been suggested previously[27,28], leads to such a large increase in the free energy of the system as to be negligible in practice[46,105]. In the presence of oxygen, on the other hand, we have the so-called "chlorinating roast"[113,123], which can be described by the overall equation

$$ZnS + 2NaCl + 2O_2 = ZnCl_2 + Na_2SO_4. \quad (3)$$

If we assume that the blue luminescence of s/a ZnS results from the dissolution of $ZnCl_2$ in ZnS, the role of oxygen is clearly to make reaction (3) possible. Hence, no oxygen is needed to bring about the blue luminescence in the cases where $ZnCl_2$ can be formed even in the absence of oxygen, e.g. when ZnS is heated in the presence of HCl or with fluxes such as $MgCl_2$.[124] The ability of $ZnCl_2$ to activate ZnS with formation of a typical s/a ZnS phosphor has been demonstrated by direct experiment[36,125]. The failure of $ZnCl_2$ to give good phosphors when used as a flux[113] has been ascribed to its volatility (b.p. 733°) and also to the fact that it is a poor mineraliser[126]. Hence it is necessary, in order to prepare efficient phosphors, to heat the material with $ZnCl_2$ either in a closed vessel[36,91] or with a flux, such as NaCl, which promotes crystal growth and also inhibits the volatilisation of $ZnCl_2$ by complex formation with the latter[46].

The effect of ZnO dissolved in ZnS is to give rise to luminescence quenching rather than to the formation of luminescence centres[36]. This, evidently, is the reason for the frequently reported[7,127,128] sharp drop in the brightness of luminescence of an s/a ZnS phosphor prepared in the air after transition from sphalerite to wurtzite, in which ZnO has a much higher solubility[39,101,113] because it, too, has the wurtzite structure. In this case it is possible to raise the intensity of the luminescence by restricting the access of oxygen[26,125] or by using chlorinating agents able to form $ZnCl_2$ without the participation of oxygen[115,124,125]. According to Riehl[120] we can envisage the formation of deep oxygen traps which act as quenching centres. However, since oxygen also causes the luminescence band to shift to longer wavelengths, it is conceivable that the oxygen becomes associated with the defect responsible for the luminescence, forming a new centre with a lower recombination coefficient[36].

For steric reasons, the Cl^- ions are unlikely to reside in interstitial sites. Hence they are most likely to replace sulphur ions in lattice sites, and in order to satisfy the principle of valency compensation the appropriate number of V_{Zn} vacancies must appear when $ZnCl_2$ is dissolved in ZnS:

$$n\,ZnS + ZnCl_2 \rightarrow Zn_{n+1}V_{Zn}S_nCl_2. \quad (4)$$

In a system of this type three main kinds of defect — $Cl_S^{\cdot}$, $V_{Zn}Cl_S^{\cdot}$, and V_{Zn}'' — can arise. As already mentioned, it has been suggested[111] that the acceptor defect $V_{Zn}Cl_S^{\cdot}$ is the one responsible for the formation of the blue luminescence centres. An analogous situation should arise when activation is by sulphides of tervalent metals, because these, too, should generate zinc vacancies when dissolved in ZnS. The association of V_{Zn}'' with a tervalent metal ion which has entered the lattice gives a centre similar to $V_{Zn}Cl_S^{\cdot}$, but in this case the ion associated with V_{Zn}'', e.g. $Al_{Zn}^{\cdot}$, will occupy a Zn site rather than an S site. Thus we can expect some difference in the spectral composition of the luminescence between s/a ZnS phosphors prepared by doping with halides and those containing tervalent metals. It has been shown experimentally[35,61] that this difference actually exists.

Thus, the "self-activated" ZnS phosphor is in fact activated by halogens or tervalent metals, i.e. by impurities which act as coactivators in ZnS–Cu and ZnS–Ag phosphors. A similar state of affairs exists in the case of CdS, which, like ZnS, does not show luminescence (and does not change its electrical conductivity) when heated with NaCl in the absence of free oxygen[36,76,91,115]. Nevertheless, CdS is activated by cadmium chloride[36,91], whose formation under ordinary conditions of heat-treatment in air has been demonstrated by chemical analysis[46].

It must be stressed that the concentration of luminescence centres in ZnS–Cl and CdS–Cl phosphors, and even more so the intensity of luminescence, do not necessarily vary in parallel with the concentration of Cl in the sulphide phase, although in some cases such parallelism has been observed[31,125]. We must remember firstly that some of the Cl may not be at lattice sites but on internal surfaces of the crystallites[64,129], secondly that only Cl associated with V_{Zn} gives rise to luminescence centres (the extent of association depending on the temperature of heat-treatment and on other preparative conditions), and lastly that the luminescence yield is determined not by the concentration of luminescence centres but by the ratio between this concentration and the concentration of quenching centres, the latter also being a function of the preparative conditions[125]. Therefore the reported[106–108,129] lack of agreement between the concentration of Cl determined by chemical analysis and the luminescence intensity cannot be used as an argument to refute the above ideas. The fact that the sulphide phase contains, in addition to Cl, cations originating from the flux (or from its interaction with ZnS and atmospheric

oxygen[67]) does not provide grounds for doubting[64] that Cl enters the lattice at lattice sites, as many workers have confirmed (see Section II).

In recent years many new data in keeping with the Prener–Williams model have been reported[110,130,131]. The development of a method for growing single crystals of ZnS from the melt has made it possible to use Feofilov's polarisation method[132] to study the nature of the luminescence centres in crystals belonging to the cubic system. Shionoya and coworkers[130,133] have shown that the observed anisotropy of the luminescence and its dependence on the properties of the exciting radiation are consistent with the hypothesis that the luminescence centre in a ZnS–Cl crystal has a characteristic C_{3v} symmetry, as should be the case with a $V_{Zn}Cl'$ centre. The e.s.r. method gave similar results[110,134-136]. When the crystal is excited at 77°K with ultraviolet radiation, ionisation of the luminescence centres and electron capture by the traps takes place. As a result, both defects become paramagnetic, and give a signal from whose characteristics we can derive information on the symmetry of the corresponding centre and on whether the signal is the result of electron capture or hole capture. A parallel study of the magnitude of the signals and of the luminescence intensity can identify which of the two signals corresponds to the luminescence centre. An analysis of the results obtained for ZnS–Cl and ZnS–Al phosphors has shown that the Prener–Williams model is consistent with the e.s.r. measurements.

The views described here have found numerous supporters. It must be stressed, however, that the chemical nature of the blue luminescence centres in s/a ZnS phosphors is one of the points of greatest disagreement. In particular, many workers restate outdated opinions that self-activation is actually present in this case, some[15,137-142] following Schleede's original views[6] in regarding the luminescence centres as formed by a stoichiometric excess of Zn or Cd, while others[143,144] adopt the opposite view, and suggest, following Bube[107,108], that the luminescence centres are formed by zinc vacancies. Schleede himself[91] gave convincing arguments against activation by excess zinc or cadmium, and abandoned his original point of view (though more gradually than did Kröger): he found that, after being heated in a sealed tube, ZnS gives a bright luminescence if $ZnCl_2$ is present as well as an excess of sulphur, whereas the characteristic luminescence of "self-activated" phosphors does not appear if the Zn or Cd is in excess. Other workers[36,127,139] also obtained negative results in their attempts to induce luminescence by an excess of Zn or Cd. The lack of luminescence of ZnS heat-treated in hydrogen[15,30,118,125] is evidence of the same kind. According to a number of reports[35,36,61], no luminescence is obtained also on heating ZnS and CdS prepared by precipitation and completely free from chlorine, whether or not an excess of sulphur is present. Work on the preparation of ZnS films by synthesis from the ultrapure elements[145] has confirmed that departures from the stoichiometric composition cannot give rise to the blue luminescence. These observations cannot be ascribed to imperfections in the crystal structure, because, as already pointed out, addition of a mineraliser such as NaCl does not induce luminescence in the complete absence of oxygen[113-115,146]. Furthermore, a hydrogen atmosphere, which inhibits the development of luminescence, favours the recrystallisation of ZnS.[22] Lastly, the most perfect single crystals of ZnS and CdS, prepared by sublimation of the precipitated sulphides, very often do not show luminescence[76]. The relative instability of s/a ZnS and s/a CdS when heated in a vacuum[14], on which Riehl and Ortmann have cast doubt[118], can be explained by the volatility of $ZnCl_2$ and $CdCl_2$. In the light of these results, there are no grounds for attempting to explain the "gap" in the luminescence intensity in the series of s/a ZnS–CdS(hex.) phosphors at 5–10% CdS by postulating the displacement of the emission band due to excess zinc by the cadmium band[14,138], especially since a similar "gap" (though less marked) is found also in the series of ZnS. .CdS(hex.) phosphors activated by Ag, Cu, and Au.[53,147].

The luminescence of sulphides not containing deliberately added activators is usually due either to the presence of activating impurities (in particular Cl) in the sulphide source material or to impurity pick-up from the walls of quartz crucibles[148,149]. Technical "phosphorescent" ZnS and CdS usually contain an appreciable amount ($\geq 0.005\%$) of chloride[36,76,113,135,150], which is readily coprecipitated with sulphides[151,152] or derived from absorption of HCl, a common constituent of the atmosphere in chemical laboratories and workshops. Both the importance[21] and the difficulty[153] of removing chlorine have long been stressed in the literature. Even when the material is synthesised from the elements it is necessary to guard against the presence of activating impurities, in particular In, Ga, and Al.[154]

Thus, there is still no convincing experimental proof of the hypothesis that the blue luminescence of ZnS or the corresponding red luminescence of CdS can be ascribed exclusively to structural defects, and the term "self-activated" is retained for phosphors of this type largely on grounds of tradition.

The green luminescence displayed by ZnS under certain conditions of heating in the absence of deliberately added metal activators[23,91,155-157] has attracted less attention. It is observed most often when the sulphide is slightly oxidised. Leverenz, noting the similarity between this luminescence and the green emission of ZnS–Cu, suggested that the true activator in all cases of luminescence of this type is oxygen, the only function of the copper being to promote the oxidation of ZnS.[23] This hypothesis, however, does not account for the observed activation by copper in the absence of oxygen[32]. Bundel'[155] also suggested that oxygen can act as an activator, but he did not identify the oxygen centres with those responsible for the green luminescence of ZnS–Cu. An important aspect of this problem is the fact that this effect is shown only by free oxygen in amounts insufficient to cause extensive oxidation of ZnS. We may therefore assume that the activating effect of oxygen shows itself in the initial stages of its reaction with ZnS. The suggestion has been put forward[36] that this initial stage consists in addition of oxygen to ZnS with formation of a defect of effective charge -2, i.e. a cation vacancy adjacent to an oxygen atom in an anion site:

$$n\mathrm{ZnS} + {}^1/_2\mathrm{O}_2 \rightarrow \mathrm{Zn}_n\mathrm{V}_{\mathrm{Zn}}\mathrm{OS}_n. \qquad (5)$$

Other workers also have assumed that oxygen reacts with zinc in the first instance[22,158]. Kröger holds the opposite opinion[101]. He explains[159] the green luminescence band of a preparation heated in zinc vapour, not in terms of zinc vacancies, V_{Zn}, but, on the contrary, by the presence of an excess of zinc in the lattice, thus resorting to the oldest explanation[2,8] of the blue band of s/a ZnS phosphors. Other authors[36,91,139], however, failed to confirm these observations. Browne[156], referring to experiments by Hamilton on the heat-treatment of CdS in sulphur vapour, considers that the green band of ZnS and

the corresponding band of CdS are due to cation vacancies. Kulp[160] expressed a similar opinion with respect to CdS. However, the preparation by this method of ZnS with green luminescence has not been confirmed[36,61,116]. It is obvious that further experimental work with careful control over copper and oxygen impurities is needed to solve the problem of the true nature of the green luminescence centres, since this luminescence has been observed also in sublimed phosphors[143,145] and in single crystals[150,161].

Many workers[15,116,145,162,163] have reported also the appearance of an orange and a red luminescence in ZnS free from deliberately added metal activators‡. The only suggestion put forward to explain this phenomenon is that an excess of sulphur can induce luminescence[116].

In addition to the bands situated on the long-wavelength side of the blue band of s/a ZnS phosphors, and of the corresponding red band of s/a CdS, short-wavelength bands have also been reported[59,164-167], in particular a band having λ_{max} = 380–390 nm with ZnS [59] and 580 nm with CdS,[98,166] observed on excitation of the phosphors at low temperatures. Kröger[164] ascribed this band in ZnS to the Na^+ cation of the flux, assumed to form a luminescence centre analogous to Cu'_{Zn} and Ag'_{Zn}. However, as shown by Rothschild[59], the same band can be obtained also in the absence of Na^+. The condition for the predominance of this band in the spectrum is that the concentration of Cl or other halogen in the ZnS phase shall be low enough. This is achieved, for instance, by heat-treatment in an atmosphere which almost suppresses the chlorinating roast[59,105]. However, this luminescence band also disappears when the "coactivators" are completely removed. According to Rothschild, the role of luminescence centres in this case is played by the "coactivator" ions, which replace sulphur ions in the lattice: these are defects which give rise to electron traps. We may suppose that a decrease in the concentration of Cl causes the ratio $[Cl_S]/[V_{Zn}Cl_S^{\cdot}]$ to increase, owing to dissociation of $V_{Zn}Cl_S^{\cdot}$. This, besides lowering the probability of electron emission from the trap when the temperatures fall, increases the probability of radiative recombination of a trapped electron with a free hole in the valency band. This is evidently a specific case of the scheme (Fig. 2*b*) proposed by Klasens to explain the long-wavelength emission of phosphors containing tervalent metals as coactivators (see above). Consequently, there is no sharp boundary between trapping centres and luminescence centres[168], and the coactivators are in fact activators in this case as with the blue self-activated luminescence, because they determine the spectral composition of the radiation. It has been suggested[169,170] that sulphur vacancies may also be a cause of the luminescence at 380–390 nm. However, direct experiments with sulphides which had been dechlorinated in hydrogen sulphide failed to confirm this suggestion[105]. The effect of heat-treatment in zinc vapour on sulphides containing chlorine, which is to increase the contribution of the short-wavelength band to the emission spectrum[170], can be explained by a shift towards the right-hand side in the equilibrium

$$V_{Zn}Cl' \rightleftarrows V''_{Zn} + Cl,$$

caused by the interaction of V''_{Zn} with $V_S^{\cdot\cdot}$ formed under these conditions of heat-treatment. This results from the fact that the product of the concentrations of V''_{Zn} and $V_S^{\cdot\cdot}$ must be constant. The role of excess zinc may also be to influence the occupancy of the Cl levels by electrons.

Perhaps the only radiation which cannot be eliminated by even the most thorough purification of the sulphides is the so-called "edge-emission"[171-173], observed mostly at low temperature and consisting of a series of narrow bands close to the edge of the absorption band of the main lattice. Most of the work on this type of luminescence has been done on cadmium sulphide. Essentially, there are at least two "edge emissions", lying in the green and the blue regions of the spectrum in the case of CdS. Kröger[171] ascribed the green radiation to interband transitions in the undisturbed lattice. However, this interpretation had to be abandoned for two reasons: firstly, the energy of the quanta corresponding to the green radiation is less than the width of the forbidden gap[172,174], and secondly the green luminescence is strongly affected (even in the absence of emission bands in the visible and infrared regions) by the preparative conditions, the most perfect single crystals with the smallest number of structural defects being free from this luminescence[36,175-177]. There are reports[76,91,141,178-180] that the green band can occasionally be observed in the photoluminescence spectrum of CdS single crystals and powders even at room temperature, particularly in the case of activation by metallic indium[105], and that an excess of cadmium enhances the effect[91,181]. On the other hand, it is stated[142] that single crystals showing green luminescence have a high resistance, whereas an excess of cadmium in the lattice should raise the electrical conductivity. Some workers[182,183] have ascribed the green luminescence to an excess of sulphur. The view that the defects responsible for the green luminescence are pairs of vacancies of the two kinds ($V_{Zn}V_S$) has become increasingly popular in recent years[97,184]. The fact that a strong green luminescence is occasionally observed at room temperature suggests that the defects responsible for this effect are located at special sites in the crystals, most probably at the surface[105] or at dislocations[185]. Several observations[186,187] may indicate that even the short-wavelength component of the edge emission is ultimately produced by structural defects, possibly localised just below the crystal surface[187]. Thus, only the edge radiation can with sufficient justification be linked with centres produced by self-activation.

IV. LUMINESCENCE CENTRES OF COPPER- AND SILVER-ACTIVATED PHOSPHORS

The theoretical concepts discussed in Section II provide a satisfactory description of the structure of one luminescence centre in the ZnS–Cu phosphor. In fact, the nature of this phosphor is far more complex. In the visible region of the spectrum alone, four emission bands — blue, green, yellow, and red — have been observed[25,188]. Three emission bands have been found in the infrared region[156].

Much of the work has been concerned with the origin of the green and blue emission bands. As a rule, an increase in the copper content initially enhances the green luminescence at the expense of the blue luminescence of "self-activated" ZnS, but subsequently the blue luminescence again predominates over the green[17,25,32], and the phosphor begins to develop a grey colour. This has led a number of authors[19,71,115,189] to suggest that the copper is simply precipitated from the ZnS lattice as a separate phase,

‡ We are not concerned here with the yellow and red fluorescence often observed in precipitated ZnS and in ZnS which has been heated below the normal temperature of formation of the crystal phosphor.

with restoration of the ability of the "self-activation" centres to emit radiation. According to several workers [190-193], however, this hypothesis conflicts with observed differences between the properties of the bands in question. The blue copper band, when it can be clearly resolved from the green band by suitable preparative or excitation conditions, occurs at significantly shorter wavelengths, and is appreciably narrower, than the blue self-activated band [45,190,192]. On decreasing the temperature the Cu band shifts to shorter wavelengths, and the self-activated band to longer wavelengths [45,61,193,194]. Phosphors with a strongly developed blue Cu band, unlike the self-activated phosphors, have a sharp characteristic absorption band [32,193,195,196] and a corresponding blue luminescence excitation band [197,198]. It must be noted that, with phosphors prepared by conventional techniques in air, the blue and the green bands are poorly resolved in the luminescence spectrum at room temperature. This evidently accounts for discrepancies [189,193,198,199] between various measurements of absorption and excitation spectra. Hence the following facts provide more convincing evidence of a difference in chemical nature between the defects responsible for the formation of "blue" luminescence centres in ZnS–Cu and in s/a ZnS phosphors: (1) when ZnS–Cu(NaCl) is heated in hydrogen a strong blue luminescence appears, whereas when a copper-free charge is heated under otherwise identical conditions no luminescence is obtained [192], because the chlorinating roast of the ZnS is suppressed; (2) introduction of Cu into s/a ZnS phosphors at relatively low temperatures (290–550°) enables the gradual displacement of the self-activated band by the blue Cu band to be monitored [193].

Another question which has been the subject of lively discussion is the mechanism of the enhancement by oxygen, established by many workers [101,200-203], of the formation of the "green" luminescence centres. Grillot and Bancie-Grillot [128,200-202] assumed that the difference between the "green" and the "blue" centres is determined essentially by their environment: if they consist of sulphur ions exclusively a blue luminescence centre is formed, whereas if an oxygen ion is present in the immediate vicinity of the Cu^+ a green luminescence centre is formed. These views are not very different from those of Konstantinova-Schlezinger [204-206], who considers the luminescence centre to be a complex (quasi-molecule) formed by an activator ion with the anions surrounding it. Grillot's explanation conflicts, however, with the fact that ZnS–Cu phosphors showing a strong green luminescence can be prepared from deoxidised ZnS even in an atmosphere which contains no oxygen, such as dry HCl. [32,116] Grillot's more recent suggestion [207] that a V_S vacancy (rather than an oxygen ion) is the neighbour of Cu^+ which can alter the nature of the centre is also unable to explain these facts, particularly since a hydrogen atmosphere, which should favour the formation of V_S, leads to enhanced blue, not green, luminescence in ZnS–Cu. [25,192] Kröger [208] points out that, when NaCl is used as a flux, only the blue luminescence is produced in the absence of oxygen, and suggest that oxygen can somehow assist the separation of Cl from Na. The mechanism of this effect of oxygen has subsequently been clarified [67,124] by thermodynamic calculations: CuCl is not formed by the direct interaction of Cu_2S and NaCl, since the process would involve a large increase in the free energy of the system, but in the presence of oxygen CuCl can be formed by a chlorinating roast similar to reaction (3). This explanation is of limited application, however, since cases are known in which oxygen assists the formation of "green" centres even in the absence of chloride fluxes [101]. Kröger points out that oxygen has a similar effect on the formation of ZnS–Ag phosphors, which he explains on the basis of the principle of volume compensation [101], assuming that the small volume of the O^{2-} ion (as compared with S^{2-}) favours the entry into lattice sites of Cu^+ ions, which are larger than Zn^{2+}. Unlike Cl^-, the oxygen ion appears as a nearest neighbour of Cu^+, but this causes only a slight shift of the green band of the Cu^+ centre to longer wavelengths, rather than converting a blue centre into a green centre, as postulated by Grillot. The same principle was later used to explain the favourable effect of $MgCl_2$ on the formation of ZnS phosphors [124]. It is possible, on the other hand, that the true mechanism of the reported effect of ZnO, which is specially evident in the case of ZnS(hex.)–Cu, consists in the formation of additional structural defects of the dislocation type, which assist diffusion into the bulk of the lattice [36]. To some extent, this could also be the role played by chlorinating agents.

When Cu_2S is dissolved in ZnS containing ZnO, valency compensation is achieved (at least partly, if chloride is present) by sulphur vacancies, which give rise to trapping centres. Furthermore, the higher electronegativity of oxygen as compared with sulphur should cause the zinc atoms situated next to oxygen atoms to become trapping centres. Hence we can expect a sharp change in the nature of the thermal glow curves if the phosphor is prepared in the presence of oxygen. Experiments have shown [84,85] that this effect actually occurs.

Many investigations have been devoted to determining the nature of the Cu blue luminescence centres. The fact that the blue luminescence appears at high copper concentrations suggests that the centres are associated. Riehl and Ortmann arrived at this conclusion from their experiments on the introduction of copper at a relatively low temperature (450°) into s/a ZnS or ZnS–Cu phosphors which had been previously heated at a high temperature [209]. Since the blue luminescence band appears only after the copper concentration exceeds a definite limit, they suggest that this limiting concentration is determined by the concentration of point defects generated in the previous high-temperature treatment ("acceptors"), and able to take up copper with formation of "green" centres. This model recalls Smekal's early views [210]. Noting, in common with other workers, that chlorides promote the appearance of green luminescence and raise the limiting concentration of copper, Riehl and Ortmann ascribe the effect to the desulphurising action of chlorides, leading to the formation of V_S vacancies, which, as originally suggested [118,203], are associated with a neutral Zn atom located at a regular lattice site. Replacement of the Zn atom by a Cu atom produces a "green" centre. If the concentration of copper exceeds the concentration of $Zn_{Zn}V_S$ defects, the excess of copper goes into interstitial sites with formation of blue luminescence centres $Cu_i Cu_{Zn} V_S$, where the subscript i denotes an atom in an interstice. Subsequently [13], taking into account the results of magnetic susceptibility measurements on ZnS–Cu phosphors, Riehl and Ortmann modified their views and admitted that the whole of the copper is present in the lattice as Cu^+, the blue luminescence centre being formed by the association of Cu_i^+ with a "green" centre, i.e. a Cu^+ ion at a lattice site. However, they retained their assumption regarding the desulphurising action of chlorides, and ascribed to the resulting sulphur vacancies the function of charge compensation. Having observed that heating even at temperatures of the order of 100–200° converted green centres into blue centres, which did not require charge compensation according to their

new model, they were faced with the problem of explaining the fate of the sulphur vacancies during this conversion. This led them to yet another hypothesis [13,211], according to which charge compensation is ensured by interstitial Zn_i^{2+} ions during formation of the "green" centres. The conversion of "green" centres into "blue" centres involves exchange of places between Cu^+ and Zn_i^{2+} ions, accompanied by the formation of $Cu_i^+Cu_{Zn}^+$ associations. This idea has found the support of other authors [191,212-214], despite the fact that it became necessary, for example, to postulate blocking of interstices [212] by Zn_i^{2+} ions to explain the failure of some ZnS–Cu phosphors to accept additional quantities of copper at low temperature with formation of "blue" centres. (It may be recalled that the number of free tetrahedral cavities is equal to the number of lattice sites occupied by zinc ions.) We could list a number of phenomena which cannot be explained satisfactorily within the limits of Riehl and Ortmann's theory. This applies primarily to the role of chlorides. Their suggested desulphurising action still lacks convincing experimental proof [215,216], and is inconsistent with the results of a thermodynamic analysis [119]. The exact role of this factor is also obscure if charge compensation is achieved by interstitial Zn_i^{2+} ions. Furthermore, as has already been pointed out, an atmosphere of H_2, known to assist desulphurisation, favours the formation of "blue" rather than "green" centres [25,192]. Also unexplained is the appearance of red luminescence in ZnS–Cu phosphors prepared in the absence of coactivators and oxygen [148,188]. In their more recent papers [13,211,217,218] Riehl and Ortmann admit the possibility of charge compensation by chlorine, and also of reactions of type (6) (see below), but they have not yet modified their model accordingly.

In an attempt to reconcile the assumption of associated blue luminescence centres with the fact that these centres are not formed when ZnS–Cu is heated in H_2S in the absence of coactivators, Kröger [219] concluded that phosphors showing blue luminescence are produced by dissolution of the subchloride Cu_2Cl in ZnS. To make the idea more concrete, he put forward a model according to which the "blue" centre arises as a result of association between a Cu^+ ion at a lattice site and a neutral Cu atom in an interstitial site. In support of his model, Kröger quotes the results of a chemical analysis which shows that the concentration of Cu in phosphors with a blue luminescence band is double the Cl concentration, and also some approximate thermodynamic calculations in agreement with experiment. It was found, however, that an atmosphere of sulphur vapour favours the appearance of blue luminescence [91,190], which makes the presence of free atoms seem unlikely, particularly in view of the diamagnetic nature of the centres [71]. A more accurate chemical analysis, allowing for the fact that part of the copper is on the surface of the crystals [45], showed that $[Cu]:[Cl] < 2$, and in many cases approaches unity. A kinetic study of the formation of ZnS–Cu phosphors on heating in a chloride flux in the presence of air showed that the appearance of a blue luminescence band is preceded, as a rule, by the green luminescence: this led to the hypothesis [67,124] that the formation of "blue" centres is a secondary process occurring in the ZnS phase after dissolution of CuCl and consisting in an atomic rearrangement leading to the association of two Cu^+ ions in adjacent cation sites of the lattice. This process can be envisaged as a preliminary to the formation of Cu_2S as a separate phase, as shown by the equation [67,192]

$$2\,(CuCl) + ZnS \rightleftarrows (ZnCl_2) + (Cu_2S), \qquad (6)$$

(where the symbols in brackets denote species dissolved in the ZnS phase), resembling the reaction between AgCl and ZnS which occurs on the surface of ZnS–Ag phosphors [46]. The fact that HCl must be present for blue luminescence to appear on heating in H_2S [32] is explained, on this model, by the solubility of CuCl in ZnS being greater than that of Cu_2S; thus, since the $ZnCl_2$ formed by reaction (6) remains in the lattice, Tomlinson's analytical results [45] are readily explained. When ZnS–Cu is heated in H_2, a treatment which gives rise to sulphur vacancies, entry of Cu_2S occurs by the scheme

$$Zn_nS_{n-1}V_S + Cu_2S \rightarrow Zn_{n-1}Cu_2S_nV_S + Zn, \qquad (7)$$

similar to the one proposed earlier by Riehl and Ortmann for the formation of "green" centres.

Later researches [192,193] showed that conversion of the "green" centres in ZnS–Cu,Cl phosphors into "blue" centres usually occurs at relatively low temperatures (below 250°). The favourable effect of quenching on the green luminescence and of slow cooling on the blue luminescence had been pointed out earlier by Rothschild [25]. Some authors [220-222] regarded the increase in the blue luminescence at the expense of the green as an irreversible process ("aging" of the phosphor), but it has been shown [13,192,223,224] that heating at 250–300° restores the green luminescence. According to Riehl and his coworkers [13,211], who heated the phosphor in a vacuum, this conversion of blue into green luminescence is irreversible unless it is carried out in a closed, evenly heated space. However, experiments with ZnS–Cu, Cl phosphors prepared with a chloride flux in air have indicated [192] complete reversibility of the interconversion of "green" and "blue" centres even when the process is carried out in an open vessel at atmospheric pressure. If we assume that the reaction can be described by Eqn. (6) or that it somehow involves the association of Cu^+ ions into pairs and the dissociation of these pairs, we are faced with the problem of suggesting how the necessary movement of ions in the lattice can occur so readily below the Tammann temperature. Riehl's hypothesis of the diffusion of Cu^+ ions through interstices is no real answer, because, as was stated above, it does not explain why diffusion occurs in some cases and not in others. The suggestion that dislocations play an important part in these processes is more reasonable [192,198]. There has been a growing realisation in recent years that many phenomena observed in crystal phosphors [144,225-229] are controlled by the presence of dislocations. The diffusion of activators in ZnS at low temperatures is probably one of these phenomena. This is confirmed by the observation [230] that single crystals with a high dislocation density can take up abnormally large amounts of Cu. Riehl and Ortmann point out [190] that in diffusion experiments of this type the "blue" centres behave as intermediate states, since prolonged heating results in conversion of the "blue" centres into "green" centres. Wendel [212] drew attention to the fact that often the appearance of blue luminescence goes hand in hand with the electroluminescent properties of the phosphors, and attempted to relate both phenomena to the presence of Cu^+ in interstices, despite the numerous reported instances of blue luminescence not accompanied by electroluminescence [193]. However, all these observations help to establish an interrelation between the various sets of phenomena: one possible explanation is based on the assumption that dislocations play an important part both in the formation of "blue" centres and in the erection of the barriers needed for electroluminescence. Kinetic studies of the conversion of "green" centres into "blue" centres [231] support the suggestion that the process consists in the "expulsion" of Cu^+ ions to remote regions of the dislocation field, where Cu'_{Zn}–Cu'_{Zn} dimer formation takes place as indicated by Eqn. (6). These

dimers can be regarded as an intermediate state between single Cu^+ ions and more or less coarse agglomerations of these ions around dislocations, known as "Cottrell atmospheres" (since ZnS and Cu_2S are not isomorphous, the latter tends to appear in regions where the lattice is disturbed[232,233]). The segregation of Cu^+ ions around dislocations under certain conditions gives rise to the barriers to which the electroluminescent properties of ZnS–Cu phosphors are attributed. Thus, both the formation of "blue" centres, arising from defects of the Cu'_{Zn}–Cu'_{Zn} type, and the electroluminescent properties result from the process which precedes the precipitation of copper from the ZnS lattice as a separate Cu_2S phase. This hypothesis is consistent with the fund of experimental data obtained in the investigation of electroluminescent materials[193,212,225,234]. The study of phenomena such as the diffusion of activators and in particular the low-temperature interconversion of luminescence centres has shown a need for a wider application of the new concepts, which are now relegated to a separate branch of science — the chemistry of the defect solid state.

In addition to the views considered above, there are others on the nature of the Cu centres giving rise to blue luminescence. According to Curie[235,236] it is the "green", not the "blue", centres which have an associated structure comprising both activator and coactivator ions. But the association of Cu^+ and Cl^- should be enhanced by increasing the concentration of Cu^+, leading to conversion from blue to green luminescence, which is at variance with the facts. Nor is this hypothesis consistent with the fact that the spectral position of the green luminescence band is independent of the nature of the coactivator[237].

It has been suggested[45,156] that the blue and the green luminescence bands belong to a single centre having two levels, the difference between phosphors with blue and with green luminescence arising, according to Browne[156], from differences in the occupancies of these levels. An attempt was made to interpret the infrared luminescence of ZnS–Cu phosphors from this point of view. Essentially, Browne identifies the "blue" and the "green" centres of "self-activated" phosphors with those of copper-activated phosphors, and ascribes a decisive role to the zinc vacancies. We have already listed the arguments against identifying in this way centres of different kinds. In general, this seems an unlikely standpoint from which to attempt to explain the great variety of facts relating to the influence of preparative conditions on the optical properties of phosphors.

Some complications arise from the fact that the blue Cu band is again displaced by the green band as the concentration of copper is increased[32]. This happens under conditions which give a fairly high solubility of Cu in ZnS.[198] Several workers[32,45,71] point out that the green bands corresponding to a low ("green-I") and to a high ("green-II") concentration of copper have the same shape and occupy the same position in the spectrum. The slight differences observed by other authors[106,236] may be due to incomplete resolution of the blue and the green band, to the formation of a Cu_2S filter on the surface of the phosphor, to the faster conversion of wurtzite into sphalerite when the phosphor is cooled in the presence of high concentrations of copper[238], and to the influence of ZnO in the ZnS lattice on the position of the maximum and on the half-width of the band. There is some evidence[198] that the excitation spectra of the green-I and the green-II bands are identical, although even this question involves divergence of opinion[199], no doubt resulting from the influence of preparative conditions. Studies of the temperature dependence of the luminescence suggest[32,45,52,71] that the appearance of a green-II band in place of the blue luminescence band is caused by a fall in the temperature of incipient quenching of both bands under the influence of an increase in the concentration of quenching centres: as a result, the blue luminescence band ceases to be observable at room temperature. The quenching centres can be more or less coarse aggregates of Cu^+ ions[124,222], whose formation within the ZnS phase becomes possible only at high enough concentrations of dissolved Cu. Thus, the green-II band does not appear when the Cu is introduced by diffusion at 450°,[239] or when ZnS–Cu is heated in H_2 or ZnS–Cu, Al is heated in H_2S.[198] Hence there are grounds for regarding the green-I and the green-II bands as identical, produced by the same luminescence centres, in spite of the fact that some anomalies[198] in the behaviour of phosphors showing a green-II band are still unexplained.

According to Froelich[188,240] and others[61,63,148,241-243], it is possible to prepare a ZnS–Cu phosphor with a red luminescence band (λ_{max} = 670–720 nm) in an atmosphere of H_2S at relatively high Cu concentrations (optimum 0.1%[188]), when the system has been rigorously freed from coactivators and oxygen. It has been suggested that the "red" centres, like the "blue" luminescence centres, are formed by the association of two Cu atoms[148,188]. Froelich believes that, in the absence of coactivators which stabilise the Cu in the Cu^+ state, the copper is more readily reduced to neutral copper atoms, which can then form red luminescence centres by becoming associated with Cu^+. However, this hypothesis is inconsistent with the lack of paramagnetic properties of the "red" centres[71]. Aven and Potter[148] have suggested that Cu^+ is oxidised to Cu^{2+} under the influence of the S_2 produced by the dissociation of H_2S. Two Cu^{2+} ions at neighbouring cation sites undergo charge transfer and form a $Cu'Cu^{\bullet}$ red luminescence centre. This hypothesis is not consistent with the fact that phosphors having a red luminescence band are not formed in an atmosphere of sulphur vapour. van Gool and Shionoya ascribe the decisive role to another product of the dissociation of H_2S — hydrogen — since they believe that hydrogen can penetrate ZnS[241] or form sulphur vacancies[242], whose association with Cu^+ gives rise to red luminescence centres. This hypothesis, however, conflicts with their own experimental finding that no red luminescence is produced by heating in H_2, and also with reports of red luminescence in phosphors heated in CS_2[188,244] in the absence of H_2. Furthermore, a $Cu_{Zn}V^{\bullet}_S$ centre should be compensated by a Cu'_{Zn} centre giving green emission, but this has not been observed. Bowers and Melamed[71], having found a blue and a red luminescence band in the same sample, made the suggestion that the Cu^+ is displaced into interstitial sites, the resulting cation vacancy acting as the blue luminescence centre, whilst the Cu^+ ion accounts for the red emission. However, other workers have shown[148,241,242] that the appearance of red luminescence is by no means invariably accompanied by the blue luminescence band.

Presland et al.[245] obtained ZnS–Cu phosphors with yellow and red luminescence by rapidly cooling (quenching) the phosphor after heat-treatment in hydrogen sulphide or argon. The effect was not inhibited by the presence of a chloride flux. A subsequent low-temperature heat-treatment at first increased the relative contribution of the red band to the spectrum, and then produced the usual blue and green luminescence. These workers[245] suggested that the excess of Cu remaining in the ZnS lattice after quenching perturbs the levels of the "blue" and "green" centres, con-

verting them into "yellow" and "red" centres respectively. The possibility of producing ZnS–Cu phosphors with a yellow (λ_{max} = 590 nm) and a red luminescence in the presence of Cl has been mentioned also by Vlasenko [90] and Kazankin [193]. It has recently been shown [231] that a ZnS(hex.)–Cu phosphor with strong yellow and red bands in its luminescence spectrum can be prepared also in the presence of oxygen by heating the phosphor at 145–150° for 10–30 min after it has been heated in the air with a chloride flux and quenched. In contrast to the findings of Presland et al., the "quenched" phosphor had a green luminescence, which became yellow and then red only after low-temperature baking. The same result was obtained [246] in a study of "quenched" phosphors prepared in a medium of HCl + H_2S. An interpretation of these observations is [231] that, in the absence of coactivators and oxygen, and if the heating conditions do not favour the formation of sulphur vacancies, one-half of the Cu^+ ions remain in interstitial sites when Cu_2S is dissolved in ZnS. The tendency of Cu_2S to be precipitated as a separate phase induces a tendency for the interstitial Cu_i^+ ions to combine with Cu_{Zn}^+ ions located at lattice sites. At high enough copper concentrations (~ 0.1%) this process occurs even in the presence of coactivators and oxygen, but the latter promote the transfer of Cu^+ ions to lattice sites during cooling. However, if the phosphor is "quenched" and then baked at a low temperature, it is possible to freeze the intermediate state corresponding to the formation of Cu_i^+–Cu_{Zn}^+ associations; these are evidently responsible for the formation of luminescence centres, the "yellow" and the "blue" centres corresponding to different extents of association.

An analysis of the published data reveals a large measure of similarity in the physicochemical behaviour of ZnS–Cu and ZnS–Ag phosphors, although some of the phenomena are less easy to observe in the case of ZnS–Ag. This is clearly because the large size of Ag^+ makes it difficult to achieve sufficiently high concentrations of activator and the formation of associations in the ZnS phase. At high Ag concentrations and low amounts of coactivator, a short-wavelength band is observed (λ_{max} = 620 nm in CdS and 380–395 nm in ZnS). [247-251] Although a band close to this one has also been observed in phosphors not containing Ag, and has given rise to the suggestion [169] that the emission is due in both cases to sulphur vacancies, the slight difference in the position of the two maxima [98], and especially the effect of baking on the spectrum of the CdS–Ag phosphor with a short-wavelength luminescence band [231,248], indicate that the centres responsible for this band may be similar to the "blue" centres in ZnS–Cu phosphors. Heat-treatment of ZnS–Ag in H_2S in the absence of coactivators and oxygen gave [148,252,253] an orange luminescence band (λ_{max} = 620–640 nm), evidently similar to the red band in ZnS–Cu. The effect of the nature of the activator on the spectral composition of the luminescence of these phosphors, and also the disappearance of these bands at low concentrations of Cu or Ag, suggest a causal relationship between luminescence centres and activator. Although e.s.r. measurements point to the presence of defects of the type $Ag_{Zn}^{\cdot}V_S^{\cdot}$ in these phosphors [252], there is no convincing proof that these are the defects responsible for the luminescence centres. There are some isolated reports [53,254,255] of a weak greenish-blue band (λ_{max} = 480–495 nm) in the luminescence spectrum of ZnS–Ag phosphors, recently confirmed by the work on "quenched" phosphors, in whose spectrum this band is most clearly visible [231]. The similarity in physicochemical behaviour (disintegration of the centres on low-temperature baking) suggests that the "green–blue" Ag centres and the "yellow" Cu centres are alike. The corresponding centres in CdS–Ag give a band with λ_{max} = = 780 nm. [256,257] In the light of what has been said in this and in the previous Sections, we can conclude that, notwithstanding statements to the contrary [97], the luminescence centres formed by silver usually give radiation of shorter wavelength than the corresponding "copper" centres (see Table).

TABLE. *Defects most likely to be responsible for the formation of the luminescence centres in various ZnS phosphors. (The maxima of the corresponding emission bands are shown in brackets).*

Wavelength scale, nm		400	450	500	550	600	650	700
Spectral region		ultraviolet	violet	blue	green	yellow	orange	red
Phosphor	ZnS–Cl	$Cl_i^{\cdot}$ (380-390)	$V_{Zn}Cl_S^{\cdot}$ (450-465)	$V_{Zn}O_S^{\cdot\cdot}$ (510-520)				
	ZnS–Ag	$Ag_{Zn}^{\cdot}$–$Ag_{Zn}^{\cdot}$ (380-395)	$Ag_{Zn}^{\cdot}$ (435-450)	$Ag_{Zn}^{\cdot}$–$Ag_i^{\cdot}$ (480-495)			$Ag_{Zn}^{\cdot}$–$Ag_i^{\cdot}$ (620-640)	
	ZnS–Cu		$Cu_{Zn}^{\cdot}$–$Cu_{Zn}^{\cdot}$ (440-450)	$Cu_{Zn}^{\cdot}$ (515-530)	$Cu_{Zn}^{\cdot}$–$Cu_i^{\cdot}$ (570-590)			$Cu_{Zn}^{\cdot}$---$Cu_i^{\cdot}$ (670-720)

V. "INDIRECT" ACTIVATION AND STRUCTURE OF THE LUMINESCENCE CENTRES

It should be evident from the previous Sections that attempts to explain the great variety of properties of the sulphide phosphors on the assumption of a unique state of the activators in the sulphide lattice (atoms in interstices, ions with an effective charge of -1 at lattice sites, etc.) have proved fruitless. It is also clear that luminescence bands having similar positions in the spectrum are often due to centres produced by defects of different chemical origin, and attempts to attribute them to one and the same centre are groundless. It appears that the wealth of properties of zinc sulphide phosphors depends on the fact that defects, formed by a large number of different impurities and by their combinations with one another and with structural defects, can give rise to luminescence centres, which is not the case with other classes of phosphors. The fundamental cause of this phenomenon is a question that theory must answer.

In the preceding pages we have discussed the chemical nature of the defects responsible for the formation of luminescence centres. But there is another side to the problem under discussion; does the electronic transition responsible for the act of emission occur in the impurity atom (or ion), or does it occur in its immediate vicinity, consisting of atoms of the host material? To solve this problem we must first of all note that the luminescence centres become ionised during the excitation of luminescence. This is shown by the bimolecular nature of the luminescence of ZnS phosphors [258], and by the internal photoeffect which accompanies the luminescence. It was the need to adopt a model which would give a relatively small (about 3 eV) excitation energy for the luminescence centres which caused Seitz [2] to put forward his original hypothesis that the phosphors are activated by free atoms which have penetrated to interstitial sites in the lattice. However, this hypothesis soon came into conflict with the facts, and was displaced by new concepts, according to which the blue luminescence centres in ZnS–Ag and the green luminescence centres in ZnS–Cu are formed by Ag^+ and Cu^+ ions occupying sites of the host lattice. But this

made it necessary to deny that the activator species themselves become ionised, because not only are the ionisation energies of Ag^+ and Cu^+ an order of magnitude higher than those of the corresponding luminescence centres, but they are in the reverse order to the relative quantum energies of the emitted radiation actually found[83,85]. Starting from an ionic model of a crystal phosphor, Klasens[83] suggested that the electronic transitions responsible for the act of emission take place between ions of the main compound. The deficiency of positive charge at a site occupied by a univalent activator assists the removal of electrons from neighbouring S^{2-} ions, and this gives rise to a localised level above the valency band. Even earlier, Leverenz[23] had explained the gradual shift in position of the luminescence band of (Zn, Cd)S phosphors on increasing the concentration of CdS by suggesting that the radiation is emitted by the sulphur atom. Klasens claims support for these views in the fact that replacement of S by Se leads not only to a shift in the luminescence band to longer wavelengths, arising from the smaller width of the forbidden gap, but also to the appearance of a new luminescence band[14,83], which can be ascribed to a perturbed selenide ion. In conformity with the lower electronegativity of Se as compared with S, this band occurs at a longer wavelength than does the corresponding band in the ZnS phosphor. In a similar way the trapping centres can be considered to be Zn^{2+} ions perturbed by neighbouring atoms of the coactivator or by V_S. In agreement with this theory, replacement of Zn^{2+} by Cd^{2+} leads to the appearance of a new trapping level. The small differences in spectral position of the luminescence bands associated with centres of different chemical nature argue in favour of the hypothesis that the electronic processes giving rise to luminescence occur in structural elements of the host lattice. We are now discussing the so-called "indirect activation"[259], which leads to the formation of localised levels which are not characteristic of specific activators.

In the electrostatic approximation the level of S^{2-} adjacent to a defect of charge -1 should lie at a height of $\epsilon = e^2/Kd = 0.74$ eV, where e is the electronic charge, $K = 8.3$ the dielectric constant of ZnS, and $d = 2.35$ Å the interionic distance. Attempts have been made to explain the dependence of the energy level of the centre on the nature of the activator in terms of the polarising effect of the latter, but no rigorous and universally applicable quantitative theory has yet emerged[85]. This has produced a tendency to abandon the ideas of Klasens[47,61]. Thus, Kröger[47] considers that holes localised on excited centres must spend part of their time in the electron shell of an impurity. This point of view is essentially similar to the above-mentioned ideas of Konstantinova-Shlezinger[204], who regards the centres as quasi-molecules. One development of the tendency to explain all the various properties of ZnS phosphors in terms of a single model was Broser's attempt[98] to construct a hydrogen-like model of the luminescence centre. However, the identification of the particular structural elements of the crystal phosphor in which the radiative electronic transitions take place remains an open question.

The experimental material discussed in the preceding Sections provides several illustrations of the similarity between the emission spectra of phosphors containing luminescence centres of entirely different chemical, electrical, and structural nature. This argues in favour of the assumption that the luminescence is caused by electronic transitions in the host material. However, any theory based on this hypothesis must take cognisance of the fact that the bond in ZnS and CdS is predominantly covalent. Therefore the valency electrons taking part in transitions belong not just to sulphur atoms but to both S and Zn (or Cd) atoms. This means that a molecular model of the luminescence centre is a better approximation than an ionic or an atomic model for phosphors of this class. Observations which suggest that molecularly disperse sulphides can luminesce in approximately the region of the spectrum where most of the luminescence bands of normal crystalline sulphide phosphors appear lead to the same conclusion. Thus, according to Weyl[260] and Vargin[261], the yellow luminescence of glasses coloured with cadmium sulphide is due to molecularly disperse CdS, as shown in particular by the absence of a crystalline phase in the glasses with the brightest emission. Gurvich[262,263] found that the dissolution of small amounts of CdS and ZnS in melts of $CdCl_2$, $CdBr_2$, and mixtures of these salts with $ZnCl_2$ produces phosphors having a strong luminescence; this can be explained by electronic transitions in molecules of CdS and ZnS held in the gap between the layers of atoms of the cadmium and zinc halides, which form a layered structure. Several other luminescent systems have been prepared whose ability to emit light can be ascribed to activation by CdS molecules distributed in the bulk or on the surface of the phosphor substrate[260,264,265]. Atoms of Cd (Zn) and S can interact, of course, not only among themselves but also with other neighbouring atoms, but the bond between Cd (Zn) and S is so different in character from all other bonds that we can speak of the formation of CdS and ZnS molecules: this difference accounts for the fact that these molecules are energetically isolated, a necessary condition for the development of luminescence. In a sulphide crystal the bonds between S and Cd (or Zn) atoms adjacent to a defect in the crystal lattice are different, owing to the perturbation caused by the defect, from the bonds in the unperturbed regions of the crystal, and thus we can again use the term molecules or quasi-molecules, formed by the atoms of the sulphide nearest to a defect. Electronic transitions in quasi-molecules of this type, responsible for the act of emission, could be likened to transitions in isolated molecules in a vapour (unfortunately, very little is known about the properties of these molecules[266]) or in solution, for example in the solid solutions discussed above. Since the S–Zn bond is strongly polarised[65,66], the cloud of valency electrons being mainly around the S atom, replacement of Zn by Cd does not have such a marked effect on the luminescence as has replacement of S by Se. This is the case both in normal crystalline sulphide phosphors[83] and in halides activated by sulphides[263]. The relative closeness of a quantum of the characteristic radiation of the majority of centres to the width of the forbidden gap in the sulphide, and the very important close interaction between the electronic processes taking part in the luminescence centres and in the lattice of the host material, are natural consequences of the fact that the phosphor matrix and the luminescence centres are composed of atoms of the same elements. Thus, the capacity for luminescence is embedded, as it were, in the sulphides themselves.

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ALUMINIUM HYDRIDE

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I. INTRODUCTION

Aluminium hydride is one of the least studied but most interesting hydrides and also one of the most interesting in practical respects.

The detailed investigation of aluminium hydride and its complexes can give results of considerable significance for the further development of ideas about the nature of the chemical bond in molecules constructed from atoms of light elements.

Aluminium does not react directly with hydrogen to form the simple hydride AlH_3. Reactions which would yield pure (individual) aluminium hydride by the hydrogenation of aluminium compounds or by exchange reactions with other metal hydrides in the absence of a solvent which is a donor of electrons are still not known. In practice one is usually dealing with solutions or precipitates containing onium complexes of aluminium hydride with oxygen- or nitrogen-containing molecules. When these complexes are sufficiently stable (for example, those with tertiary amines $AlH_3.NR_3$) they can be isolated from the reaction mixture and obtained in an individual state.

The sharp rise in reactivity of the compounds of aluminium in relation to hydrogenating agents in the presence of a solvent which is a donor of electrons is due to additional ionisation of the Al–X bond owing to the effect of an electronic shift in the formation of the onium bond:

Furthermore, complex formation with a solvent stabilises the hydride molecule formed by the reaction:

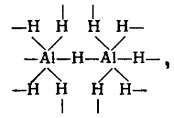
$$AlX_3 + 3MH \rightarrow AlH_3 + 3MX,$$

"clearing" the electron deficiency at the metal atom and hindering polymerisation, which leads to the formation of unstable, insoluble $(AlH_3)_x$.

The valence capacities of aluminium towards hydrogen are not determined uniquely. In alkali metal tetrahydroaluminate complexes† aluminium apparently has a coordination number of six. In support of this assumption there is the absence of isomorphism between $NaAlCl_4$ and $NaAlH_4$. According to Baenziger[1], $NaAlCl_4$ is orthorombic, with tetrahedral $AlCl_4^-$ ions at the lattice sites.

† Termed *alanates* in the Russian, presumably as derivatives of "alane", the name suggested by Wiberg for the AlH_3 unit (Ed. of Translation).

Such "ions" are either absent from the sodium tetrahydroaluminate lattice, being bound in an infinite pattern:



or are so distorted that their departure from tetrahedral symmetry leads to a different type of packing of the molecules in the crystalline lattice. From the formal point of view, octahedral coordination of the hydrogen atoms or ions around the aluminium atoms is entirely possible but the value of this conclusion, drawn on the basis of a comparison of the r_{Al}/r_H ratios with the known criteria for the stability of polyhedra with coordination number four or six, is quite relative, owing to the uncertainty in estimating the radii of the aluminium and hydrogen atoms which are specific for just this type of interaction. On the other hand, a series of derivatives of aluminium hydride are shown in which aluminium exhibits, formally at least, the coordination number of five.

Bis(trimethylamine)alane [2-trimethylamine-aluminium hydride (Ed of Translation)] $AlH_3.2N(CH_3)_3$ and the polymeric *NN'N*-tetramethylethylenediaminealane [*NN'N*-tetramethylethylenediamine-aluminium hydride (Ed. of Translation)] $AlH_3.Me_2N[CH_2]_2NMe_2$ are the only compounds of aluminium hydride for which there have been exhaustive X-ray diffraction investigations[2,3].

The bis(trimethylamine)alane molecule has a trigonal bipyramidal configuration with the hydrogen atoms situated in the equatorial plane. In the linear grouping N–Al–N the interatomic distance d_{Al-N} is 2.18 ± 0.01 Å, that is, a little greater than in aluminium nitride (1.87 Å) and considerably greater than the sum of the covalent radii (1.96 Å).

The configuration of a trigonal bipyramid with the aluminium atom at the centre of the equatorial plane is also retained in the compound of aluminium hydride with *NN'N'*-tetramethylethylenediamine. The interatomic distance d_{Al-N} is 2.195 ± 0.05 Å, and the valence angle N–Al–N is somewhat less than 180°.

It is interesting that in trimethylaminegallane $GaH_3.N(CH_3)_3$, the molecule of which apparently has a configuration[4] identical with that of $BF_3.N(CH_3)_3$, d_{Ga-N} = 1.97 Å, agreeing well with the sum of the covalent radii of Ga and N.

Apparently the increase in the coordination number of aluminium to five or six can be linked either with the participation of the 4*s*- and 3*d*-orbitals in bond formation or with a considerable ionicity of one of the Al–X bonds in the complex. In the latter instance there is some analogy with the so-called "quinquevalent" nitrogen.

II. METHODS OF MAKING ALUMINIUM HYDRIDE AND ITS AMINE COMPLEXES‡

It was mentioned above that there is not yet a method for isolating "pure" unsolvated aluminium hydride from a reaction mixture.

Attempts to obtain it by a "dry" method (without use of a solvent) have been unsuccessful or are of only theoretical significance.

In the direct reaction of metallic aluminium with hydrogen at 1500°, only physical adsorption of the gas takes place.[5] When an aluminium wire is vaporised in an atmosphere of hydrogen at 1100°, a product is formed in which the H:Al ratio fluctuates from 0.19 to 1.02.[5] It is suggested that under these conditions a mixture of aluminium and polymeric aluminium hydride is formed, but the properties of this product differ markedly from those of polymeric aluminium hydride, obtained from ethereal solution — all the hydrogen is lost on heating to -78° whereas the "ordinary" hydride is "stable" up to 105–110°.

The probability of the formation of aluminium hydride under these conditions was shown mass-spectrometrically[6], in which study aluminium hydride monomer was formed at low aluminium concentrations (~ 0.43%) at ~ 1090°, and the formation of the dimeric molecule Al_2H_6 was observed at ~ 1170° and a higher aluminium concentration (~ 1.7%).

On treating an aluminium–cerium alloy (up to 14% Al) with hydrogen, a product is formed which shows a thermal effect at ~ 210–230° on pyrolysis.[7] Decomposition on the walls of the ampoule gives a faint metallic mirror; as cerium hydride decomposes at a much higher temperature, this effect may be connected with the decomposition of aluminium hydride.

The reduction of trimethylaluminium by hydrogen in an electric discharge leads to the formation of aluminium hydride[8,9], but in this instance a mixture of alkylaluminium hydrides and aluminium hydride is obtained.

Methods based on the reduction of aluminium compounds with various reductants in a solvent–electron donor medium have the greatest practical importance for obtaining solutions of polymeric "solvated" aluminium hydride.

1. Reduction of $AlCl_3$ by lithium hydride in ether[10,11]:

$$AlCl_3 + 3LiH \xrightarrow{20^\circ} AlH_3 + 3LiCl.$$

This reaction proceeds in two stages: initially lithium tetrahydroaluminate is formed, which with an excess of aluminium chloride gives aluminium hydride. As a result of the reaction a metastable solution of aluminium hydride in ether is formed, from which on standing the hydride is deposited as a polymer $(AlH_3)_x$.

2. Reduction of aluminium chloride by lithium tetrahydroaluminate in ether[12,13]:

$$AlCl_3 + 3LiAlH_4 \rightarrow 4AlH_3 + 3LiCl.$$

The yield of aluminium hydride here is considerably greater than in the previous method.

3. Reduction of aluminium chloride by calcium or magnesium hydrides with added aluminium in ether.[14] The yield of aluminium hydride is almost quantitative, according to information in the patent.

4. Reaction of aluminium chloride with diethylaluminium hydride in ether[15]:

$$AlCl_3 + 3Et_2AlH \rightarrow AlH_3 + 3AlEt_2Cl.$$

The yield of aluminium hydride is ~ 70% and depends on the time for carrying out the reaction since increasing the duration of the process increased the yield of a side-product of composition Al_2H_5R.

‡ For the latter, see also J.K.Ruff, "Nitrogen Compounds of Boron, Aluminium, Gallium, Indium, and Thallium", Chapter VI of "Developments in Inorganic Nitrogen Chemistry, Vol.1" (Edited by C.B.Colburn), Elsevier, Amsterdam, 1966 (Ed. of Translation).

5. An electrolytic method for obtaining aluminium hydride by the reduction of a saturated solution of sodium tetrahydroaluminate in tetrahydrofuran at a mercury cathode was recently patented.[16] After electrolysis for three hours, the Al:Na ratio was 2.7; it could be taken that the $NaAlH_4$ concentration had decreased and the aluminium hydride had been formed.

All attempts to desolvate aluminium hydride obtained from ethereal solutions have been unsuccessful. On heating, loss of ether molecules does not take place, but the Al–H bond is broken, and when a freshly prepared solution is treated with a large quantity of inert solvent (pentane or ligroin) an etherated product of composition $(AlH_3)_n \cdot (C_2H_5)_2O$, where $n = 2.05-2.30$, is obtained[17].

The isolation of aluminium hydride from the reaction mixture and its stabilisation could be effected by treating it with substances which are stronger donors of electrons than diethyl ether. Such substances are amines forming stable amine complexes, which (unlike the oxonium solvates) are individual substances of constant composition.

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The following methods for obtaining complexes of aluminium hydride with amines are possible:

1. Direct reaction of solvated aluminium hydride with amines[18–20].

2. Reaction of an ethereal solution of aluminium hydride with the gaseous amine (trimethylamine)[8,9,12,13,21].

3. The exchange reaction of a simple amine complex of aluminium hydride (for example, $AlH_3.NMe_3$) with more complex amines[22–25].

4. The reaction of lithium tetrahydroaluminate with the amine hydrochloride.[26]

5. Direct reaction of lithium tetrahydroaluminate with the amine in ether[27]; the yield of the complex in this reaction is very small, however.

6. The reaction of aluminium, hydrogen, and amine in tetrahydrofuran under hydrogen pressure with heating.[28]

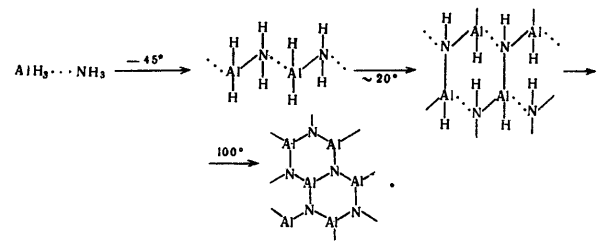
1. Compounds of Aluminium Hydride with Ammonia and Its Derivatives

The study of the reaction of aluminium hydride with ammonia began with attempts to obtain a compound analogous to borazole.[18]

On mixing a solution of aluminium in tetrahydrofuran with dry ammonia in equimolecular proportions at -80° and then heating the mixture, all the intermediate compounds analogous in composition to boron compounds were isolated, but pure alazole was not detected; the explanation given was that aluminium, unlike boron, does not tend to form Al⇄N double bonds, owing to the less electrophilic nature of the "incomplete" 3*p*-orbital.

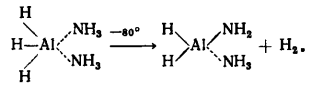
Initially at -80° a voluminous precipitate of composition $AlNH_6$ is formed, which evidently contains alazane $AlH_3 \ldots NH_3$, above -45° one mole of hydrogen is released with the formation of a highly polymeric alazene $(\ldots AlH_2-NH_2\ldots)_x$, which in turn on prolonged heating to room temperature loses a second mole of hydrogen and is converted into a highly polymeric alazyne $(\ldots AlH-NH\ldots)_x$. The formation of aluminium nitride with release of a third mole of hydrogen does not go to completion even on heating to 100°. All the products obtained are insoluble in an excess of the solvent.

In its entirety this process can be represented by the following scheme:



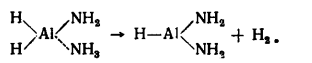
It must be noted that the release of hydrogen from the analogous boron derivatives takes place with much greater difficulty (at higher temperatures)[29,30]. The ease with which hydrogen is released from an aluminium atom was explained by its stronger electronegativity in the hydride compounds of aluminium.[18]

When aluminium hydride in ethereal solution reacts with ammonia in the molar ratio $AlH_3 : NH_3 = 1 : 4$ at -80°, an aminoalane ammine $AlH_2(NH_2).NH_3$ is formed.[18] Here the reaction evidently passes through the stage of formation of aluminium hydride–2-ammonia, $AlH_3.2NH_3$, which at the temperature of the experiment immediately loses one mole of hydrogen (above -30° almost all the hydrogen is lost):



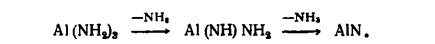
When the reaction is carried out in similar proportions at -50° a white solid of composition $AlH(NH_2)_2$ is obtained after distilling off the excess of ether.

This suggests that diaminoalane is formed by the loss of one mole of hydrogen from aminoalane monoammine:

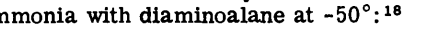


On heating this compound to room temperature, another mole of hydrogen is released, as a result of which a compound of composition $Al(NH)NH_2$ is formed.

Aminoalane and diaminoalane are intermediate products in the preparation of triaminoalane [aluminium amide, $Al(NH_2)_3$ (Ed. of Translation)], which is formed in the reaction of aluminium hydride with ammonia (in the proportions $AlH_3 : NH_3 = 1 : 4$) at -30°.[13,18] However, under such conditions of carrying out the reaction the theoretical atomic ratio of Al : N = 1 : 3 could not be reached. At best, the ratio Al : N = 1 : 2.84 was attained. On raising the temperature above -30°, triaminoalane decomposes to form aluminium nitride:



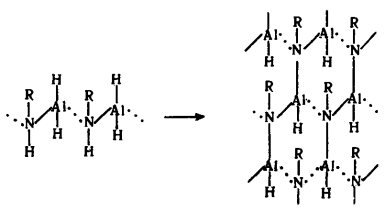
Pure triaminoalane is obtained by the reaction of an excess of liquid ammonia with diaminoalane at -50°:[18]



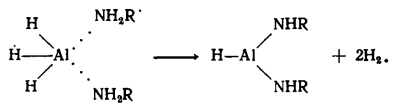
Aluminium hydride in ethereal solutions reacts with methylamine as with ammonia.[18]

When the reaction is carried out with a 1 : 1 molar ratio of the reagents in boiling dioxan a highly polymeric methylalazyne $(AlH-NR)_x$ is formed, and not a trimeric molecule corresponding to *N*-trimethylborazole. The conversion takes place in stages with the formation of *N*-methylalazane (methylamine–alane) $AlH_3 \cdot NH_2R$ and polymeric *N*-methylalazene (methylaminoalane) $(-AlH_2-NHR-)_x$.

When the reaction is carried out at -55° in ether, there is first a white precipitate of methylamine–alane $AlH_3 \cdot NH_2R$, which at -35° releases one mole of hydrogen to form methylaminoalane $AlH_2(NHR)$, converted at room temperature into *N*-methylalazyne with loss of one mole of hydrogen (released only on boiling with dioxan). All the substances thus obtained are high polymers; they are insoluble in ether and benzene and lose hydrogen with difficulty — especially in the last stage, owing to the formation of a complex network structure.



In the reaction of aluminium hydride with methylamine in ether at a reagent molar ratio of 1 : 2 and -55°, a white precipitate of $AlH_3 \cdot 2NH_2R$ is formed[18], which loses two moles of hydrogen at -35° to give bis(methylamino)alane:



Loss of the third mole of hydrogen to form Al(NHR)NR is extremely difficult, owing to the high degree of polymerisation of bis(methylamino)alane.

Bis(methylamino)alane and (methylamino)alane are intermediates in the production of a methyl derivative of triaminoaluminium, tris(methylamino)alane $Al(NRH)_3$,[18] which is a white, highly polymeric substance formed on mixing an ethereal solution of aluminium hydride with an excess of methylamine (~ 1 : 4):

$$[AlH_3] + 3NH_2R \longrightarrow Al(NHR)_3 + 3H_2.$$

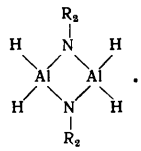
The best result is obtained by cooling the reaction mixture to -50°. The whole reaction scheme is:

$$[AlH_3] + 2NH_2R \longrightarrow AlH_3 \cdot 2NH_2R \xrightarrow{-H_2} AlH_2(NHR) \cdot NH_2R \xrightarrow{-H_2}$$
$$\xrightarrow{-H_2} AlH(NHR)_2 \xrightarrow{+NH_2R} AlH(NHR)_2 \cdot NH_2R \xrightarrow{-H_2} Al(NHR)_3.$$

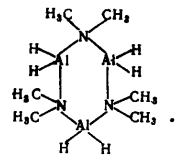
On mixing an ethereal solution of aluminium hydride with dimethylamine in the molar rato $AlH_3 : NHR_2 = 1 : 1$ at -30° and then warming to room temperature, hydrogen is liberated and (dimethylamino)alane AlH_2NR_2 is formed[18]:

$$[AlH_3] + NHR_2 \longrightarrow AlH_2(NR_2) + H_2.$$

This is readily purified by distillation in a vacuum at 40–60°. An ebullioscopic measurement of the molecular weight in ether showed that (dimethylamino)alane is dimeric and its structure evidently corresponds to the formula:



However, a cryoscopic determination of the molecular weight in benzene showed[26] that the degree of association is not 2.16,[18] but 2.99, therefore the formation of a trimeric molecule must be proposed, in which the aluminium atom has a coordination number of four and the association takes place by formation of Al–N bonds (by analogy with boron compounds[31]):



This substance melts without decomposition at 89–90°, is soluble in benzene and ether, and reacts vigorously with water with liberation of hydrogen.

(Dimethylamino)alane can be obtained by reaction of trimethylamine–alane with tris(dimethylamino)alane[32]:

$$2AlH_3 \cdot NMe_3 + (NMe_2)_3Al \rightarrow 3AlH_2(NMe_2) + 2NMe_3$$

and by reaction of lithium tetrahydroaluminate with dimethylamine in equimolecular proportions[27].

(Di-isopropylamino)alane and (diethylamino)alane are obtained in the reaction of the corresponding dialkylammonium chlorides with lithium tetrahydroaluminate[26,32]:

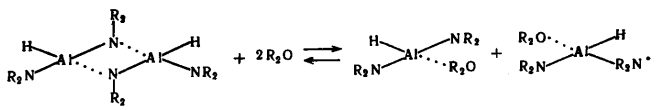
	M.p., °C	Sublimation temp., °C	Degree of association
$[(CH_3)_2CH]_2NAlH_2$	130–131	90	2.16
$(Et_2N)AlH_2$	42	—	2.12

The molecular weights of the two compounds were measured cryoscopically in benzene.

On mixing an ethereal solution of aluminium hydride with dimethylamine in the molar ratio 1 : 2 at -30°, then after the liberation of hydrogen had ceased and distillation under high vacuum at 35–50°, bis(dimethylamino)alane was obtained as colourless crystals[18]:

$$[AlH_3] + 2NHR_2 \rightarrow AlH(NR_2)_2 + 2H_2.$$

According to Wiberg and May[18], bis(dimethylamino)alane melts at 63–65° and dissolves in benzene and ether. An ebullioscopic determination of the molecular weight in ether showed that the substance is partly associated into a dimeric molecule:



Hence it is thought that the introduction of the NR_2 group diminishes the tendency to polymerisation.

Bis(dialkylamino)alanes can be isolated (in high yield) from the reaction of trimethylamine–alane with the appropriate dialkylamines[32,33]:

$$AlH_3 \cdot NMe_3 + 2(Alk)_2NH \rightarrow 2H_2 + HAl(NAlk_2)_2 + NMe_3.$$

Bis(dimethylamino)alane obtained by this method has the same melting point (62°) as the compound described by Wiberg and May[18], however, the degree of its association in benzene is 2.49 (according to these authors, 1.71 in ether). The different degree of association of bis(dimethylamino)alane depending on the solvent can be explained by the formation of an ether addition compound, although it is thought[32] that the bridging bond formed by the Me_3N group is fairly stable.

Bis(dimethylamino)alane is formed also in the reaction of sodium hydride with (dimethylamino)alane[33]:

$$NaH + 2AlH_2NMe_2 \longrightarrow NaAlH_4 + HAl(NMe_2)_2.$$

The introduction of a third R_2N group suppresses the dimerisation of the molecule, according to Wiberg and May[18]; $Al(NR_2)_3$ is monomeric. Tris(dimethylamino)alane is obtained by the reaction of an ethereal solution with dimethylamine and room temperature and molar ratio AlH_3 : NHR_2 = 1 : 4. The substance sublimes in a vacuum at 60–100°, melts without decomposition at 87–88°, and reacts vigorously with water and acids.

The same compound can be obtained by other methods. Ruff[32] proposed two methods of synthesis:

(1) $$H_3Al\cdot NMe_3 + 3HNMe_2 \longrightarrow Al(NMe_2)_3 + NMe_3 + 3H_2,$$

(2) $$LiAlH_4 + 4HNMe_2 \longrightarrow LiAl(NMe_2)_4 + 4H_2,$$

(3) $$3LiAl(NMe_2)_4 + AlCl_3 \longrightarrow 4Al(NMe_2)_3 + 3LiCl.$$

Tris(dimethylamino)alane is also obtained by the reaction of tri-isobutylaluminium with dimethylamine in heptane[34]:

$$(Bu^i)_3Al + 3HNMe_2 \xrightarrow{195^\circ} Al(NMe_2)_3 + 3iso\text{-}C_4H_{10}.$$

And finally Fetter and Bartocha[25] obtained $Al(NMe_2)_3$ by the reaction of trimethylaluminium with tetramethyltetrazene. They proposed the following reaction scheme:

$$3AlMe_3 + 3Me_2HN{=}NHMe_2 \longrightarrow 2Al(Me_2N)_3 + N_2 + 6CH_4.$$

There is a considerable difference in the physical constants of tris(dimethylamino)alane obtained by various methods (see Table 1). The marked difference between the melting points of tris(dimethylamino)alane obtained by Fetter and other authors can only be explained if quite different substances were investigated. The stability of the monomeric form in ether[18,20] and the dimeric form in benzene[32] shows that tris(dimethylamino)alane can form an ether addition compound $Al(NMe_2)_3.O(C_2H_5)_2$.[32]

Tris(dimethylamino)alane reacts without a solvent with anhydrous aluminium chloride[32]; dichloro-(dimethylamino)-alane and chlorobis(dimethylamino)alane are formed:

$$AlCl_3 + 2(Me_2N)_3Al \rightarrow 3(Me_2N)_2AlCl,$$
$$2AlCl_3 + (NMe_2)_3Al \rightarrow 3(Me_2N)AlCl_2.$$

Replacement of the third NMe_2 group taking part in the formation of a nitrogen bridge does not occur.

TABLE 1.

M.p., °C	Molecular weight	Method of determination	Reference
−30	193—199	cryoscopic (cyclopentane)	25
87—88	162	ebullioscopic (ether)	18
87—89	353	cryoscopic (benzene)	32
Not given	320	cryoscopic (benzene)	34

TABLE 2.

Compound	M.p., °C	Sublimation temperature, °C	Degree of association
$(Me_2N)_2AlCl$	55—57	55	1.95
$(Me_2N)AlCl_2$	151	90	2.12

The difference in the reactivity of the bridge and terminal dialkylamino-groups was investigated in the tensimetric titration of dialkylamino-derivatives of aluminium with gaseous boron trichloride[32].

When two moles of boron trichloride are added to one mole of tris(dimethylamino)alane (under conditions such that it is dimeric, that is, a bridge bond is formed), a sharp change in vapour pressure is observed after 15 min; when an excess of boron trichloride (over three moles) is added, the change in vapour pressure occurs after 24 h. This can be explained only by a difference in the reactivity of the NMe_2 groups in tris(dimethylamino)alane.

There are other proofs of the stability of the bridge bonds formed. When (trimethylamino)alane reacts with dimethylamine, trimethylamine is quantitatively replaced by dimethylamine and hence the equilibrium of the reaction is completely displaced in favour of a compound with nitrogen bridges[33].

Tris(di-isopropylamino)alane, unlike tris(dimethylamino)alane, is monomeric[32]. This fact is apparently connected with steric hindrance to dimerisation. The difference between these compounds also appears in the conditions for their preparation — whereas $Al(NMe_2)_3$ is formed rather readily, $Al[(iso\text{-}C_3H_7)_2N]_3$ is considerably more difficult to prepare; this is linked with the necessity of breaking the nitrogen bridges in the intermediate di-isopropylamino-derivatives of aluminium — bis(di-isopropylamino)alane is dimeric.

As mentioned above, tris(dimethylamino)alane is monomeric in ether and this is apparently due to the formation of the ether addition compound $Al(Me_2N)_3.O(C_2H_5)_2$. An attempt was therefore made to obtain an amine complex of tris(di-isopropylamino)alane with trimethylamine and dimethylamine[32].

In the first instance, no reaction was observed; in the second, there was a sudden change in pressure in the system on adding two moles of dimethylamine; apparently an exchange reaction took place instead of the formation of the expected complex:

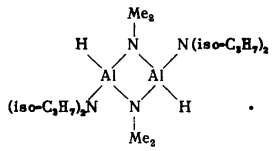
$$2(CH_3)_2NH + [(iso\text{-}C_3H_7)_2N]_3Al \longrightarrow 2(iso\text{-}C_3H_7)_2NH + (Me_2N)_2Al[N(iso\text{-}C_3H_7)_2].$$

However, (di-isopropylamino)bis(dimethylamino)alane was not isolated from the reaction products. Attempts to obtain it by the reaction of di-isopropylamine with dimethylaminoalane led to the replacement of only one hydrogen atom[32]:

$$(iso\text{-}C_3H_7)_2NH + (CH_3)_2N{-}AlH_2 \xrightarrow{36\ h} (CH_3)_2N{-}\overset{H}{\underset{|}{Al}}{-}N(iso\text{-}C_3H_7)_2 + H_2.$$

(Di-isopropylamino)(dimethylamino)alane is a solid which sublimes at 95° and its degree of association (in benzene) is 1.98. Three structural formulae for it are possible

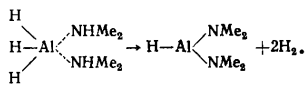
(under the conditions for the formation of nitrogen bridges), the most probable being:



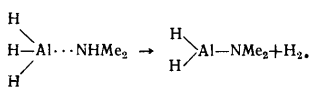
The structural formula with $(iso\text{-}C_3H_7)_2N$ bridge-forming groups is less probable, as the NMe_2 group stabilises the dimer more strongly and the molecule with a bridging bond through this group is rather stable.

As tris(di-isopropylamino)alane is monomeric and all its amino-groups are equivalent, an increase in vapour pressure is observed during tensimetric titration with boron trichloride at the molar ratio $BCl_3 : Al(NPr^i_2)_3 = 3 : 1$.[32]

To conclude this section we will consider the even less-studied bis(dimethylamine)alane and (dimethylamine)alane. Bis(dimethylamine)alane is formed in the reaction of an ethereal solution of aluminium hydride with dimethylamine at -50°.[18] It is of low stability and decomposes at -20° with loss of hydrogen and formation of bis(dimethylamino)alane:



(Dimethylamine)alane can be obtained by the action of dimethylammonium chloride on lithium tetrahydroaluminate at -40°.[26] It exists only up to -10°, above which temperature it loses one mole of hydrogen to form (dimethylamino)alane:



The amine complexes of aluminium hydride with tertiary amines in which the $[AlH_3]$ group of atoms remains unchanged are particularly interesting. Those with trimethylamine have been studied most.

These compounds are readily obtained in the reaction of freshly prepared ethereal solution of aluminium hydride with trimethylamine in the molar ratio 1:1 and 1:2 at room temperature or on coooling[8,9,12,13,20,21]. Another method of preparation is based on the reaction of lithium tetrahydroaluminate with the amine hydrochloride.[26]

Mono(trimethylamine)alane, subsequently called trimethylamine alane, distils readily in a vacuum at 60°/1 mmHg, forming colourless crystals, dissolves readily in ether, benzene, and tetrahydrofuran, reacts explosively with water, and fumes strongly in air. The pure product melts at 76° without decomposition.

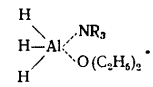
When heated rapidly to 100°, the crystals become opaque, owing to the commencement of the polymerisation of aluminium hydride:

$$x\ AlH_3 \cdot NMe_3 \rightarrow (AlH_3)_x + x\ NMe_3.$$

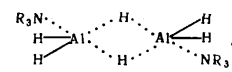
Heating on a naked flame leads to complete decomposition of the compound and the formation of an aluminium mirror:

$$AlH_3 \cdot NMe_3 \rightarrow Al + 1.5H_2 + NMe_3.$$

In determining the molecular weight (ebullioscopic method) in ether, it was found that trimethylamine alane is monomeric, but it is associated in benzene[12,13]; trimethylamine alane vapour is monomeric[35]. This difference in the behaviour of trimethylamine alane depending on the solvent was explained by the unsaturated nature of the four-coordinated aluminium atom — in ether this saturation takes place with the p-electrons of the oxygen atom:



In benzene, this propensity to saturation can be effected by the dimerisation of two molecules of trimethylamine alane with the formation of hydrogen bridges:

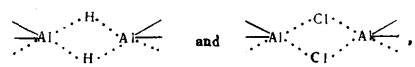


Wiberg's hypothesis of the dimerisation of trimethylamine alane received confirmation in later studies[26,36].

It can also be assumed that association of trimethylamine alane takes place by dipole–dipole interaction in the solution[36-38]. This hypothesis is based on the fact that replacement of hydrogen atoms by chlorine atoms produces a slight change in the degree of association of alane in benzene[37]:

	Degree of association
$AlH_3 \cdot NMe_3$	1.43
$H_2AlCl \cdot NMe_3$	1.32
$HAlCl_2 \cdot NMe_3$	1.46
$AlCl_3 \cdot NMe_3$	1.36

It is improbable that the stability of the rings



would be completely the same. Evidently dipole–dipole interaction is also more probable for trimethylamine alane and for an amine-complex of aluminium chloride in benzene[39].

The investigation of infrared and Raman spectra showed that the symmetry of the trimethylamine alane molecule is C_{3v} and the Al–N vibration frequency is 553 cm^{-1}.[40]

Of the other trialkylamine alanes, triethylamine alane and tri-n-propylamine alane have been obtained and studied[26,42].

Under ordinary conditions triethylamine alane is a transparent liquid, m.p. 18–19°; it is easily distilled in a vacuum at 40°.

On determining the molecular weight of this compound in benzene[26] a considerable difference from Wiberg's data[42] (determination in ether) was found. The degree of association is 1.10 according to Ruff, 1.57 to Wiberg.

With tri-n-propylamine alane steric hindrance completely prevents association into a dimer: it is difficult to distil and can be purified by recrystallisation from hexane at -80°. Its melting point is 80–81°.[26]

Bistrialkylamine alanes can be obtained by various methods which differ little in principle from one another.

When an ethereal solution of aluminium hydride is mixed with trimethylamine (1 : 2), the reaction yields a colourless solution from which, after distilling off the solvent and the excess of amine, bis(trimethylamine)alane is precipitated as a white powder; it readily sublimes in a vacuum at 30–40°/1 mmHg. The same compound can be obtained on adding an excess of trimethylamine to trimethylaminealane[13] or by the action of hydrogen chloride on lithium tetrahydroaluminate followed by addition of trimethylamine[2]:

$$LiAlH_4+HCl \xrightarrow{R_2O} H_2+LiCl+[H_3Al]\cdot R_2O,$$
$$[H_3Al]\cdot R_2O+2NMe_3 \xrightarrow{R_2O} H_3Al\cdot 2NMe_3.$$

Bis(trimethylamine)alane melts at 95° and at 100° it starts to decompose, probably with formation of a polymer of aluminium hydride and liberation of trimethylamine. The compound dissolves readily in ether, benzene, and tetrahydrofuran.

Molecular weight determinations in benzene and ether show that the substance is monomeric in these solvents[26,42]; on comparing the infrared spectra of $AlH_3.2NMe_3$ and $(AlH_3)_2(Me_2N[CH_2]_2NMe_2)_2$ it was noted that the absorption of the Al–H bond in the 5.9 μm region is the same, hence it was assumed that bis(trimethylamine)alane is partly dimerised in the gas phase[23].

Measurements of the polarisation of the molecule in benzene, cyclohexane, and dioxan did not show the presence of a dipole moment which varied in different solvents (1.2 D in benzene, 1.6 D in cyclohexane and dioxan). The existence of a dipole moment for a trigonal bipyramidal model was explained by the high atomic polarisation[38,40].

Ruff and coworkers[33] investigated the conditions for the formation and the stability of other bis(trialkylamine)alanes. The formation constants for these complexes allowed them to construct a series for the stability of alanes as a function of the alkyl group:

$$NR_3=N(CH_3)_3 > N(CH_3)_2CH_2CH=CH_2 > N(CH_3)(C_2H_5)_2 > N(C_2H_5)_3 > N(C_3H_7)_3.$$

The stability of the mixed diaminealanes changes in the sequence:

$$AlH_3\cdot N(CH_3)_3\cdot N(CH_3)(C_2H_5)_2 > AlH_3\cdot N(CH_3)_3\cdot N(C_2H_5)_3 > AlH_3\cdot N(CH_3)_3\cdot N(C_3H_7)_3,$$

that is, the stability of the complexes also depends entirely on the dimensions of the alkyl groups (mixed diaminealanes are more stable than symmetrical ones).

2. Compounds of Aluminium Hydride with Bifunctional Amines

Aluminium hydride in tetrahydrofuran reacts with hydrazine with the formation of aluminium hydrazide $Al(N_2H_3)_3$.[41] This reaction proceeds very slowly in an inert solvent whereas in tetrahydrofuran the yield approaches 94% (the isolation of this compound was carried out in a high vacuum):

$$AlH_3+3N_2H_4 \longrightarrow Al(N_2H_3)_3+3H_2.$$

The mechanism of the reaction between aluminium hydride and hydrazine is not completely clear, but it is possible that the reaction proceeds just as in the reaction of metal amides and metal alkyls with hydrazine, that is, through the formation of the ions $N_2H_3^-$ and $N_2H_5^+$, on account of a shift in the equilibrium of the protolysis of hydrazine:

$$2N_2H_4 \rightleftarrows N_2H_5^+ + N_2H_3^-.$$

The $N_2H_5^+$ ion reacts with a hydrogen ion to form a molecule of hydrazine and a molecule of hydrogen:

$$H^- + N_2H_5^+ \longrightarrow N_2H_4 + H_2,$$

and the $N_2H_3^-$ ion reacts with an aluminium ion to form aluminium hydrazide:

$$Al^{3+} + 3N_2H_3^- \longrightarrow Al(N_2H_3)_3.$$

It is interesting that in this scheme appreciable ionisation of the Al–H bond is proposed.

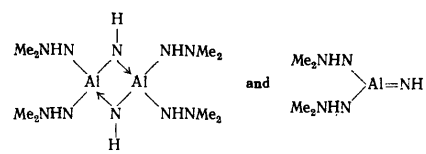
When trimethylaminealane is used instead of aluminium hydride, the reaction yields a white solid, which, when the solvent is removed, explodes at the least vibration[22]; however, this substance has not been identified.

The mechanism of the reaction of trimethylaminealane with alkyl derivatives of hydrazine and the structure of the final products of the reaction are extremely difficult to interpret and are semi-quantitative because most of the products are polymers, have a low vapour pressure, do not distil, and cannot be purified by sublimation. The direction of the reaction depends entirely on the initial proportion of the reagents, the structure of the alkyl hydrazine, and the nature of the solvent.

Methylhydrazine and trimethylaminealane (in hydrocarbon medium) give a white, stable compound[22]. On the basis of the ultimate analysis and infrared spectra of the final products the following reaction scheme was proposed:

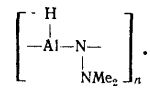
$$n\,H_3Al\cdot NMe_3 + 2n\,H_2NNHMe \longrightarrow \left[\begin{array}{l} NH—NHMe \\ |\quad\quad\quad \\ —Al—NHNMe— \end{array}\right]_n + 3n\,H_2 + n\,NMe_3.$$

1,1-Dimethylhydrazine forms with trimethylaminealane a white crystalline substance which does not sublime in a vacuum and has m.p. 193–194°.[22] Two structural formulae have been proposed for the substance:

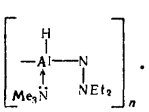


but have not been confirmed by direct experimental data, however.

When 1,1-dimethylhydrazine and trimethylaminealane in the molar ratio $Me_2NNH_2 : AlH_3.NMe_3 = 2 : 1$ react in pentane a substance with the empirical formula $C_2H_7N_2Al$ is obtained[22]. The infrared spectrum agrees best with the polymeric formula:



This structural formula is also supported by the fact that 1,2-diethylhydrazine also reacts with trimethylaminealane[22] only here the trimethylamine molecule is associated with the aluminium atom. As a result of the reaction a viscous substance is formed, the structural formula of which may be:

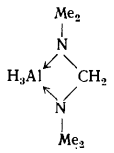


When the reagent ratio is $AlH_3.NMe_3 : Et_2NNH_2 = 1 : 1$, a white, involatile solid is formed, 1,1-diethylhydrazidoalane $AlH_2.NHNEt_2$.[22]

Trimethylhydrazine with trimethylamine–alane forms dimethylaminoalane AlH_2-NMe_2.[22]

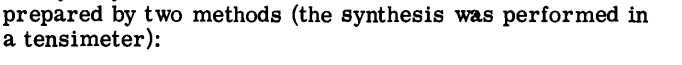
It must be pointed out that freshly prepared aluminium hydride–ether does not react with tetramethylhydrazine[22], although earlier it was thought that it has the same basicity as trimethylamine.

Trimethylamine–alane forms with *NNN'N'*-tetramethylmethylenediamine a cyclic complex which has a sharp melting point (25–26°) and is readily distilled in a vacuum at room temperature[22]. Starting from the NMR spectra and ultimate analysis the following structural formula was advanced for it:

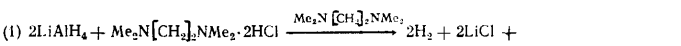


(this complex is evidently partly dimerised in benzene, where its molecular weight is 164–167, against the calculated 132).

A complex of aluminium hydride with *NNN'N'*-tetramethylethylenediamine has also been obtained[23]. It was prepared by two methods (the synthesis was performed in a tensimeter):

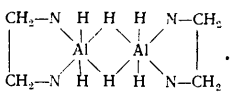


(1) $2LiAlH_4 + Me_2N[CH_2]_2NMe_2 \cdot 2HCl \xrightarrow{Me_2N[CH_2]_2NMe_2} 2H_2 + 2LiCl + 2H_3Al \cdot Me_2N[CH_2]_2NMe_2$,

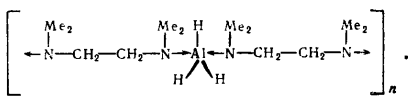


(2) $AlH_3 \cdot 2NMe_3 + Me_2N[CH_2]_2NMe_2 \longrightarrow 2NMe_3 + AlH_3 \cdot Me_2N[CH_2]_2NMe_2$.

The complex is a white solid which does not decompose on heating to 133° for 24 h. Its vapour pressure at 99.3° and 119.2° is 1.5 and 10.6 mmHg respectively. In measuring the vapour pressure it was found that the product is apparently dimeric and the probable structural formula for it with six-coordinated aluminium atoms was proposed:



However, later investigations[2,3] established the existence of associates with a linear N–Al–N bond:



The same structural formula can be proposed also for the complexes of aluminium hydride with *NNN'N'*-tetramethyl-1,3-propanediamine and 1,4-bis(dimethylamino)but-2-ene[24], since with them aluminium hydride also gives complexes of 1 : 1 composition. *NNN'N'*-tetramethyl-1,3-propanediamine–alane is a white solid with m.p. 136–140°; it distils in a vacuum at 80°/0.05 mmHg. It is obtained by the reaction of trimethylamine–alane with *NNN'N'*-tetramethyl-1,3-propanediamine[24].

The complex with 1,4-bis(dimethylamino)but-2-ene

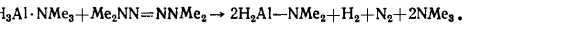
$$[H_3Al \cdot (Me_2N) \cdot CH_2CH=CHCH_2(NMe_2)],$$

is obtained by reaction with trimethylamine–alane in n-octane[24]. Its m.p. is 150–155° and it distils at 105°/0.05 mmHg. It should be noted that the investigation of these complexes has been qualitative in nature.

Fetter and Moore[24] investigated the reaction of trimethylamine–alane with tetrakisdimethylaminoethylene $[(CH_3)_2N]_2C=C[N(CH_3)_2]_2$ and hexamethylenetetramine. However, here the investigation was purely qualitative: there is no distinct chemical analysis of the product. The authors suggest that the tetrakisdimethylaminoethylene is bonded in a complex with two molecules of aluminium hydride, after which decomposition of the complex occurs (the decomposition products were not determined). The sublimation temperature of the compound is 75°.

With hexamethylenetetramine a stable complex is formed, presumably $AlH_3.(CH_2)_6H_4$, which does not sublime up to 120° and does not melt up to 200°, but above that temperature it decomposes with formation of an aluminium mirror.

The mechanism of the reaction and the end product of the reaction of trimethylamine–alane with tetramethyltetrazene has been established sufficiently accurately[25]. Tetramethyltetrazene heated in an inert solvent decomposes with formation of tetramethylhydrazine and liberation of hydrogen; however, in the presence of trimethylamine alane the dimethylamino-group does not add to the tetramethylhydrazine but reacts to form dimethylaminoalane:

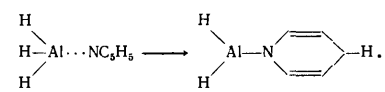


$$2H_3Al \cdot NMe_3 + Me_2NN=NNMe_2 \rightarrow 2H_2Al-NMe_2 + H_2 + N_2 + 2NMe_3.$$

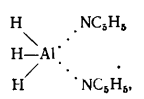
The substance was sublimed at 60°/0.005 mmHg, and then identified by melting point, ultimate analysis and infrared spectra (see above for the physical constants).

3. Compounds of Aluminium Hydride with Pyridine

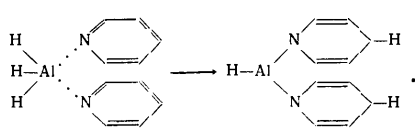
Aluminium hydride reacts in ethereal solution with pyridine in the molar ratio $AlH_3 : NC_5H_5 = 1 : 1$ at -30° with the formation of a white crystalline addition product, $AlH_3.NC_5H_5$.[19] When the latter is heated to room temperature its colour changes from white to yellow. This behaviour is explained by intramolecular rearrangements in which one atom of hydrogen connected with aluminium is introduced into the pyridine ring with formation of a compound with a quinonoid structure:



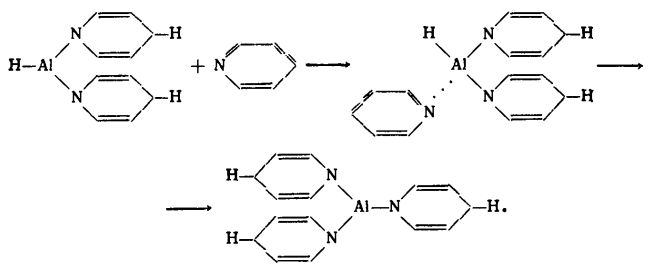
When an excess of pyridine is taken, then aluminium hydride–bis-pyridine is formed under analogous conditions:



which when slowly heated to room temperature gradually changes colour from white to dark red. During this there is considerable heat liberated and the residue melts (60–70°). This change in colour is due to the same intramolecular rearrangement:



Bis(dihydropyridyl)alane is insoluble in benzene, petroleum ether, tetrahydrofuran, chloroform, and does not dissolve in an excess of pyridine. After distilling off the excess of solvent a brownish-red solid of composition $AlH_3.3NC_5H_5$ remains[19]. Hydrolytic decomposition of this compound showed that it does not contain active hydrogen bound to the aluminium atom. Hence bis(dihydropyridyl)-alane and pyridine give tris(dihydropyridyl)alane:



The completeness of the conversion of bis(dihydropyridyl)-alane into tris(dihydropyridyl)alane depends on the reaction time. Both products are sensitive to oxygen.

4. Alkyl-Substituted Complexes of Aluminium Hydride with Tertiary Amines

In addition to the amine complexes of aluminium hydride, a series of complexes is known in which the hydrogen in AlH_3 is partly replaced by alkyl. Such compounds can be prepared as follows:

1. By the reduction of alkylhalides of aluminium with lithium hydride[43,44]:

$$R_2AlHal\cdot NMe_3 + LiH \longrightarrow R_2AlH\cdot NMe_3 + LiCl,$$
$$RAlHal_2\cdot NMe_3 + 2LiH \longrightarrow RAlH_2\cdot NMe_3 + 2LiCl.$$

2. By the alkylation of trimethylamine–alane with dialkylmercury compounds[43,44]:

$$AlH_3\cdot NMe_3 + R_2Hg \longrightarrow R_2AlH\cdot NMe_3 + H_2 + Hg,$$
$$AlH_3\cdot NMe_3 + {}^1/_2R_2Hg \longrightarrow RAlH_2\cdot NMe_3 + {}^1/_2H_2 + {}^1/_2Hg.$$

3. By disproportionations[43,44]:

$$AlH_3\cdot NMe_3 + 2R_3Al\cdot NMe_3 \longrightarrow 3R_2AlH\cdot NMe_3,$$
$$2AlH_3NMe_3 + R_3Al\cdot NMe_3 \longrightarrow 3RAlH_2\cdot NMe_3.$$

4. By alkylation of trimethylamine–alane and dimethylaminoalane with butyl-lithium[44]:

$$AlH_3\cdot NMe_3 + LiC_4H_9 \longrightarrow LiH + C_4H_9AlH_2\cdot NMe_3.$$

The reaction is complicated by a side-reaction:

$$LiH + AlH_3\cdot NMe_3 \longrightarrow LiAlH_4 + NMe_3,$$

which makes control over the stoichiometry of the reaction difficult.

The amine complexes of the alkyl hydrides are extremely sensitive to moisture and oxygen. From the little information which is available about these compounds it can be concluded that the introduction of alkyl groups into the molecule of an amine complex of the hydride stabilises the compound (Table 3).

5. Quaternary Ammonium Salts of Aluminium Hydride [Quaternary Ammonium Tetrahydroaluminates]

A paper recently appeared[45] on a new method of stabilising aluminium hydride by the formation of quaternary ammonium salts of tetrahydroaluminates.

TABLE 3.

Compound	M.p., °C	B.p., °C	Degree of association
$MeAlH_2\cdot NMe_3$	−35	25—26	1.95
$Me_2AlH\cdot NMe_3$	33—35	42—43	1.34
$EtAlH_2\cdot NMe_3$	—	35—40	1.60
$Et_2AlH\cdot NMe_3$	−28	63—65	1.18

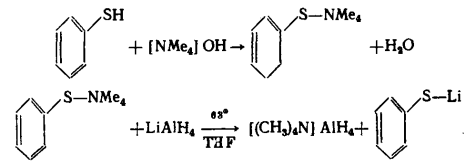
Two salts of this type have been obtained, tri-n-octyl-n-propylammonium tetrahydroaluminate, $[(C_8H_{17})_3(C_3H_7)N].AlH_4$ (I) and tetramethylammonium tetrahydroaluminate $[(CH_3)_4N]AlH_4$ (II).

They are crystalline. (I) melts at 61–63° with decomposition, and is readily soluble in benzene, toluene, and diethyl ether and poorly soluble in pentane and hexane; (II) decomposes at 173° and is not soluble in any of the organic solvents.

Both the compounds, unlike the amine complexes of aluminium hydride, exhibit great stability against hydrolysis: to complete their hydrolysis heating in 6 *N* HCl in sealed tubes for two weeks is necessary. The infrared spectra of these compounds suggest an ionic structure for their molecules. This is also confirmed for (I) by the measurements of electrical conductivity in tetrahydrofuran, which showed that the electrical conductivity of (I) is greater than (approximately twice) that of lithium tetrahydroaluminate.

The ionic character of (II) is confirmed by its insolubility in all organic solvents and by its relatively high decomposition temperature.

Compound (I) is obtained by the reaction of $[(C_8H_{17})_3.(C_3H_7)N]Br$ with lithium tetrahydroaluminate at room temperature in benzene for three days. The pure substance was isolated by treating the filtered solution with pentane. $[(CH_3)_4N]AlH_4$ was obtained by the scheme:



The substance was filtered off, washed with tetrahydrofuran and dried in a vacuum for five hours at room temperature.

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The above review shows that attention has so far been mainly directed to problems on the preparation of various derivatives of aluminium hydride. However, insufficient attention has been paid to systematic physicochemical investigation of the substances obtained.

Only two substances have been investigated by X-ray diffraction: bistrimethylamine–alane and *NNN'N'*-tetramethylethylenediaminealane; the structural formulae proposed for the other compounds are based on indirect data and are therefore not very trustworthy.

Most of the complex molecules in solution are either dimeric or trimeric, but the nature of the bonds brought about by dimerisation has been little studied; the data are contradictory and are not based on any reliable experimental evidence; there is hardly any information on the

thermodynamic characteristics of the phase transformations of the various complexes of aluminium hydride, etc.

We therefore consider that future work in the field of the complexes of aluminium hydride will be successful only if physical and physicochemical methods are widely employed.

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PARAMAGNETIC DERIVATIVES OF NITROGEN MONOXIDE

E. G. Rozantsev

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1. INTRODUCTION

Just as half a century ago, stable radicals continue to play an important part in the development of the theoretical concepts of contemporary chemical science.

The discovery and the wide use of the electron paramagnetic resonance (EPR) method was a powerful tool in the development of this field of chemistry [1-3].

Stable radicals are quite useful in solving many specific problems arising during the course of chemical, physical, and biological experiments.

This class of substances is successfully used in studying the rates of initiation of chain reactions, in catalysis, and in photochemical and quantum-chemical investigations.

After the discovery and study of the phenomenon of dynamic nuclear polarisation, stable radicals with a simple hyperfine spectral structure became used in the construction of high-sensitivity magnetometers and "Maser" type devices.

In recent years several reviews and monographs devoted to free radicals have appeared [4-12], in which little mention has been made of an important class, the paramagnetic derivatives of nitrogen monoxide.

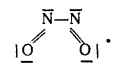
The main focus of the present review is the structure, reactivity, and methods of preparation of the compounds of this class; radiospectroscopic investigations receive less detailed consideration and problems relating to the quantum chemistry of free radicals are not discussed in this review,

2. PARAMAGNETIC NITROGEN OXIDES

The simplest free radical of this series is nitrogen monoxide:

$$\dot{N}=\bar{O}.$$

Despite the presence of a free valency, nitrogen monoxide is considerably less reactive than atomic hydrogen or chlorine and under ordinary conditions it does not dimerise, unless it is present in the liquid (b.p. -151.7°C) or solid (m.p. -163.6°C) states [13-17]. On the basis of spectroscopic investigations of solid nitrogen monoxide it can apparently be ascribed the structure [18-20]:

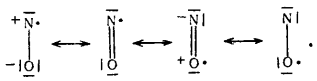


The valence state of nitrogen monoxide can be written as:

$$NO\,[KK\,(N:2s)^2\,(O:2s)^2\,(\sigma 2p)^2\,(\pi 2p)^4\,(\pi^* 2p)^1],$$

where the completely filled orbitals $(\sigma 2p)^2(\pi 2p)^4$ correspond to a triple bond, and $(\pi^* 2p)$ contains an unpaired electron. On transfer of the unpaired electron to the corresponding non-bonding orbital the NO excited species behaves as if it possessed a triple bond [21].

The thermal stability of nitrogen monoxide is so high that it does not decompose appreciably even at 500°. Pauling [22] explains the unusually low level of the ground state of the radical by quantum-mechanical resonance of four structures:



As the two partly ionic structures have approximately equal "weight", the resulting dipole moment of the species should be close to zero. The dipole moment [23] obtained experimentally was in fact very low (μ = 0.16 D).

Nitrogen monoxide can be described by a single formula using Pauling's ideas about a three-electron bond:

$$|N\overset{\cdot}{=}O|\cdot$$

The gain in energy in the formation of such a bond stabilises the species so much that the heat of dimerisation becomes negative [22]. Such a structure for the radical agrees well with the dipole moment and the measured interatomic distance, which is intermediate between the values calculated for double and triple covalent bonds [24]:

N=O	N$\overset{\cdot}{=}$O	N≡O
(1.18 Å)	(1.15 Å)	(1.06 Å)

The cation [25] and anion [26] of nitrogen monoxide have the following structures respectively:

$$[|N\equiv O|]^+\ [|\bar{N}=\bar{O}|]^-.$$

Nitrogen monoxide is a chemically active compound; it is readily reduced in solution to hydroxylamine and ammonia [27]. The gaseous reactions of nitrogen monoxide with chlorine [28,29], bromine [30], and oxygen [31] take place by three-body collisions, through a diamagnetic activated complex, for example:

$$2NO+O_2 \rightarrow [ONOONO] \rightarrow 2NO_2+27\ \text{kcal}.$$

It is interesting that when there is a very large excess of oxygen under these conditions dinitrogen trioxide is formed as the bimolecular reaction:

$$NO+NO_2 \rightarrow N_2O_3+10\ \text{kcal},$$

proceeds much faster than the termolecular reaction [32].

The high-temperature gas reaction of nitrogen monoxide with hydrogen is mainly termolecular [33], but transient states with very short lifetime produced in two-body collisions may occur [34].

Nitrogen monoxide reacts readily with other free radicals [35-38], and hence is not only an indicator [39] but also an effective inhibitor of chain reactions [40,41].

Nitrogen monoxide forms coordination compounds, the nitrosyls, with salts of iron, cobalt, and other transition metals having unpaired *d*-electrons [42-45].

Significantly, in almost all the compounds of nitrogen monoxide the additional covalent bond is formed preferentially with the nitrogen atom [46-48], which is evidence in support of the structure with a free valency at the nitrogen.

In the hyperfine structure (h.f.s.) of the EPR spectrum of nitrogen monoxide there are three transitions between four sublevels. Each line of the rotational-magnetic structure is split into triplets with a separation of ~14.2 Oe between them. Analysis of the h.f.s. parameters of the spectrum also leads to the conclusion that the greater part of the spin density (~60%) is centred on the nitrogen atom [49-52].

Nitrogen dioxide is another stable free radical of this series. The gain in energy on the delocalisation of the unpaired electron does not stabilise it enough to prevent dimerisation into dinitrogen tetroxide [53-57]:

$$2NO_2 \rightleftarrows N_2O_4+13\ \text{kcal}.$$

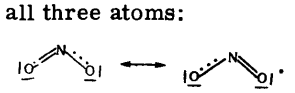
Even in the vapour (b.p. 21°C) nitrogen dioxide is partly dimerised, and in the liquid and solid (m.p. -11°C) states it is a dimer. Only at 150°C is the gas completely dissociated into nitrogen dioxide, which on further heating (~600°C) breaks down into nitrogen monoxide and oxygen [58-60]:

$$N_2O_4 \rightleftarrows NO_2 \rightleftarrows NO+O.$$
$$\uparrow\downarrow$$
$$N_2O_3$$

Sutherland and Penney [61,62] established the structure of nitrogen dioxide [61,62]. They concluded, from an analysis of the absorption bands, that the nitrogen dioxide species is not linear [63]. The molecular parameters of NO_2:

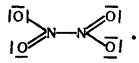
r(N—O)	∠ONO,
1.20 Å	132°

were determined by electron diffraction [64,65]. As the angle ONO is nearer 120° than 90°, it can be approximately assumed that the nitrogen atom is sp^2-hybridised and the σ-bond is formed by the use of the electrons of the molecular orbitals localised between the nitrogen and oxygen atoms. In addition to the ten electron pairs there are another three $2p\pi$-electrons which can form a three-electron bond uniting all three atoms:

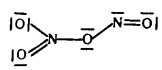


The total bond order should therefore be > 1, but < 1.5, which corresponds to a bond length of 1.20 Å. This lies between the values for the normal N–O (1.43 Å) and double N=O (1.16 Å) bonds[66-70].

X-Ray diffraction studies and data from entropy determinations support a symmetrical structure for dinitrogen tetroxide:



Since in such a structure the neighbouring nitrogen atoms have formal charges of the same sign it could be assumed that the unsymmetrical structure

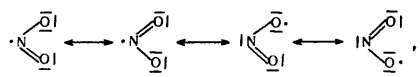


would be more stable.

The chemical properties of dinitrogen tetroxide agree better with the latter structure, as this compound can be used both for diazotisation[71] and for nitration[72].

Nitrogen dioxide is one of the most chemically active of compounds: carbon, sulphur, and phosphorus burn in it. Its free-radical nature is clearly apparent in its reactions of recombination, addition, and initiation[73-76].

Exhibiting a free valency, delocalised at the oxygen and nitrogen atoms:



nitrogen dioxide almost always displays a marked duality of reactivity in its reactions[77,78].

The EPR spectrum of nitrogen dioxide (Fig. 1) is a triplet with a separation of 47.1 Oe between the components. Such an appreciable value for the hyperfine splitting constant is apparently explained by an appreciable contribution of the s-state in the ψ-function of the unpaired electron[79]:

$$\psi = a_1\psi_N(2s) + a_2\psi_N(2p_Z) + b\psi_0(2p_Z).$$

Fig. 1. The EPR spectrum of nitrogen dioxide at 77°K.

In the best resolution of the spectrum into its hyperfine structure there is a large number of components of a rotational-magnetic structure due to independent quanta in the magnetic field of the electron-spin, nuclear-spin, and magnetic moments of the species[50,80]†

3. FREMY'S SALT‡

Over a century ago Fremy obtained a yellow salt of composition $K_2S_2O_7N$, which dissolved in water to give a purple-violet solution[81]. This salt is readily obtained by the action of lead dioxide on an alkaline solution of the corresponding hydroxylimidodisulphate[82]:

$$(KO_3S)_2NOH \xrightarrow[PbO_2]{-H} (KO_3S)_2NO.$$

The initial dipotassium hydroxylimidodisulphate can be obtained by the reaction of sodium nitrite and potassium hydrogen sulphite in aqueous solution[83]. The sodium[84], tetraphenylarsonium[85], and tetraphenylstibonium[86] Fremy salts are also known.

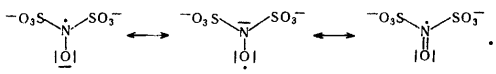
By analogy with dinitrogen tetroxide Fremy ascribed a dimeric structure to the solid salt which breaks down in solution into monomeric anions[87]:

$$(KO_3S)_4N_2O_2 \rightleftarrows 4K^+ + 2ON(SO_3)_2^- .$$

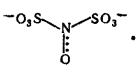
The analogy with nitrogen dioxide is well evident in the reaction of the salt with nitrogen monoxide and the reaction of the resulting addition product with water[88]:

$$(KO_3S)_2NO + NO \rightarrow (KO_3S)_2NONO,$$
$$(KO_3S)_2NONO + H_2O \rightarrow (KO_3S)_2NOH + HNO_2.$$

The bond between the oxygen and nitrogen in the Fremy ion is donor or semipolar, so that the unpaired electron is delocalised between the nitrogen and oxygen atoms of the NO group; the free ion-radical can therefore be described with the aid of several electronic structures:



In a more general form the structure of this radical can be represented with the aid of a formula including a three-electron bond:



The stability§ of Fremy's salt[90-96] in solutions is due to the low level of the ground state of the species which has a three-electron bond[97,98].

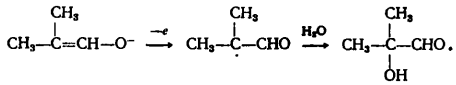
The unusual chemical properties of Fremy's salt permits its use as a selective one-electron oxidant of aromatic amines and phenols[99]. Many *ortho*- and *para*-quinone imines and quinones have been thus obtained in high yields[100-107].

† Ref. 50 is to the EPR spectrum of nitrogen monoxide. Probably Ref. 51 is intended here (Ed. of Translation).]

‡ The anion of Fremy's salt is encountered in the literature under various names: peroxylaminodisulphonate, nitrosyldisulphonate, nitrosodisulphonate, disulphonatonitroxyl, etc.

§ An aqueous solution of Fremy's salt can be kept under ordinary conditions for a few days[89].

Isobutyraldehyde is also smoothly oxidised by Fremy's salt into α-hydroxyisobutyraldehyde, the reaction passing through the stage of single-electron oxidation of the anion of the enol[108]:

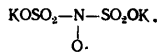


The reaction of Fremy's salt with hydrazine and hydroxylamine allows it to be used for the analytical determination of these reagents[109,110]:

$$4(KO_3S)_2NO+N_2H_4 \rightarrow 4(KO_3S)_2NOH+N_2,$$
$$4(KO_3S)_2NO+2NH_2OH \rightarrow 4(KO_3S)_2NOH+N_2O+H_2O.$$

It has been used successfully in weakly alkaline solutions as a photographic developer[111].

A mechanistic analysis of the chemical reactions suggests that almost all the radical reactions of Fremy's salt take place at the oxygen atom of the NO group, in accordance with the imidoxyl electronic structure of this radical:



The EPR spectrum (Fig. 2) of the Fremy anion (in chloroform) is a triplet with components which are equidistant and of the same intensity, the distance between them being ~13 Oe, and the breadth of each < 0.5 Oe.[112-114]. The hyperfine structure of the EPR spectrum agrees well with the theoretical expectation of interaction of the unpaired electron with the nuclear spin of the nitrogen[115]. A detailed study of the fine structure of the EPR spectrum of Fremy's salt[116-118] enabled it to be used for calibrating radiospectrometers[86].

With the discovery of the dynamic polarisation of nuclei[119-121] (the Overhauser–Abragam effect) Fremy's salt unexpectedly acquired exceptionally important practical value[122-129]. The Overhauser effect, which forms the basis of the double nuclear–electron resonance method, allows the hyperfine structure of EPR spectra of extremely dilute solutions of free radicals to be investigated in weak magnetic fields, where the usual EPR method is insufficiently sensitive.

Aqueous solutions of Fremy's salt are now being used both in the USSR and abroad for the construction of highly sensitive nuclear precession magnetometers[125-128].

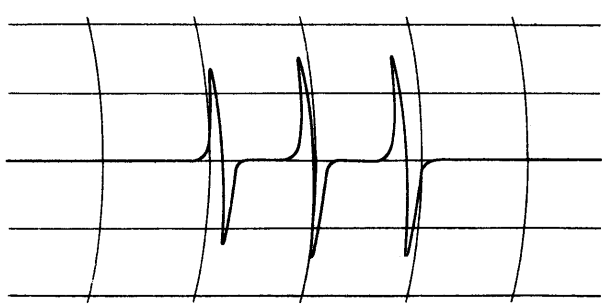
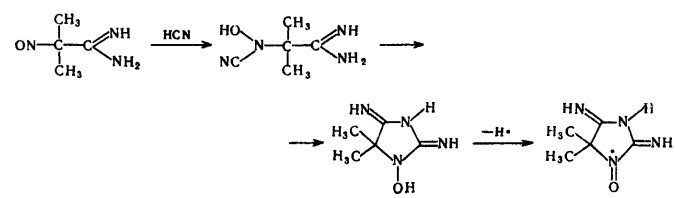


Fig. 2. The EPR spectrum of a chloroform solution of Fremy's salt.

Fremy's salt has found an important application as the working material in "Maser" type devices[129] and also for studying the nature of molecular motion and the microstructure of liquids[130] by the spin-echo method[131,132].

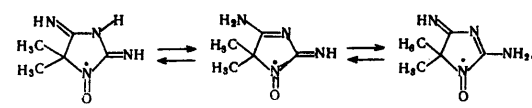
4. NITROXIDES

The paramagnetic compounds of this class are often called in the literature free radicals of quadrivalent nitrogen. The first organic radical of quadrivalent nitrogen was obtained in 1901 by Piloty and Schwerin[133] by the scheme:



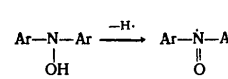
It is a brick-red substance, known as porphyrexide¶, which is reminiscent of nitrogen dioxide and Fremy's salts in its chemical properties. Moreover, porphyrexide readily displaces chlorine from hydrochloric acid, reacts with nitric acid, with alkalis, and also with chlorine to give mono- and di-chloroporphyrexides[134]. The possibility that some of these reactions take place without use of the free valency is not ruled out. Unfortunately neither the structure nor the paramagnetism of the porphyrexide derivatives was established.

Later magnetic susceptibility[135] and EPR spectroscopic studies[136,137] confirmed the free-radical nature of porphyrexide as a nitrogen(IV) compound. The EPR spectrum of porphyrexide is a triplet with a separation of 10 Oe between components, but the hyperfine structure of the components of the triplet has not been interpreted unambiguously. Hausser assumes[138] that the complexity of the hyperfine structure can be explained by the existence of an equilibrium between a few valence-tautomeric† forms in porphyrexide solutions:



In all the tautomeric structures of porphyrexide the bond between the nitrogen and the oxygen is semipolar or donor, which undoubtedly corresponds to a lower (stable) energy level due to possible formation of a conjugated diene or triene system of bonds by which the unpaired electron may be delocalised.

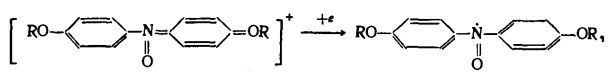
The individual diaryl nitroxides can be sufficiently reliably obtained by one of three methods — by careful oxidation of the diaryl hydroxylamines[139]:



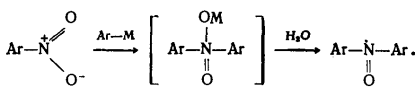
¶ Because its colour is similar to that of murexide (ammonium purpurate).

† [sic]. The author means tautomerism, not valency-tautomerism (Ed. of Translation).

by single-electron reduction of corresponding alkoxyl derivatives of the oxides of diarylammonium salts with perchloric acid [140]:



and by the action of organometallic compounds on nitro-compounds [141]:



The radicals of this class are red, crystalline compounds, stable in air. An important property of these substances is their ability to retain paramagnetism even at very low temperatures (-60°C).

The high stability of aromatic nitroxides permits their detection in a different type of oxidising system which includes aromatic amines,

Hoskins [142] observed the EPR spectrum of diphenyl nitroxide on passing oxygen through a hot mixture of toluene, alcoholic alkali, and diphenylamine. The catalytic oxidation of solutions of aromatic derivatives of naphthylamine, methylaniline, aniline, and phenothiazine also led to the appearance of corresponding EPR signals [143]. Apparently, stable nitroxides can be obtained from a large number of aromatic amines and are widely used as antioxidants and polymerisation inhibitors. EPR has been used to study the oxidation of many aromatic amines in the liquid phase [144,145]. However, it must be borne in mind that the EPR spectrum does not always give unambiguous information about the chemical structure of the oxidation product.

The preparation of the pure free radicals of this class is known to be difficult, which explains why only a few diaryl nitroxides have been isolated in the free state during the last fifty years (Table 1).

The stability of the diaryl nitroxides depends on various factors, including the electronic and steric effects of the substituents, the overall symmetry of the chemical species, the nature of the crystal lattice of the material, etc.

Of the three possible structures for diphenyl nitroxide, the first and last correspond to the maximal gain in energy due to conjugation of the nitrogen–oxygen bond with the aromatic system:

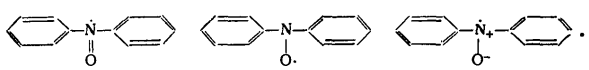
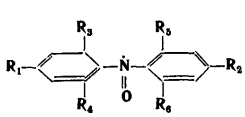
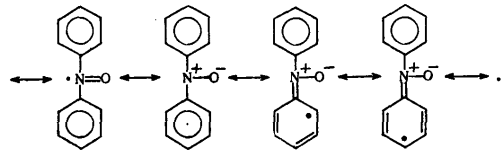


TABLE 1. Individual diarylnitroxides 

R						M.p., °C	Stability	References
1	2	3	4	5	6			
						64	days	139, 146, 147–155
CH_3	CH_3					59–60	hours	146, 147
NO_2	NO_2					109	months	146, 156
CH_3O	CH_3O					161	years	140, 146, 147, 156–171
CH_3O	CH_3O	CH_3O		CH_3O		121.5–122	unstable	140, 157, 158
CH_3O	CH_3O	CH_3	CH_3	CH_3	CH_3	163		140, 158
CH_3O	CH_3O	CH_3O	CH_3	CH_3O	CH_3	175		158
		CH_3O	CH_3O	CH_3O	CH_3O	199–200		141
CH_3O				CH_3O	CH_3O	114.5–115		141

The hyperfine structure of the EPR spectrum of diphenyl nitroxide [172] showed that it can be described with the aid of several electronic structures of covalent and ionic type, the relative contribution of which depends on the polar properties of the medium.



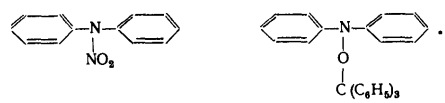
The hyperfine structure of the EPR spectrum of diphenyl nitroxide (Fig. 3) consists of three groups of lines due to the splitting of the level of the unpaired electron at the nitrogen nucleus. Each group is divided into a large number of components owing to delocalisation of the unpaired electron by the π-orbital system of the aromatic nuclei and its interaction with the protons [173].

An analysis of the spectroscopic parameters shows that ~40% of the spin density is at the nitrogen atom, 30% at the oxygen, and 30% at the *ortho*- and *para*-positions of the aromatic nuclei [153].

The dipole moments [155,174], the intensity of the colour, and the reactivity of the homologues and derivatives of diphenylnitroxide are consistent with these conclusions.

Wieland and his many students [175] have made the outstanding contributions to the study of the reactivity of diaryl nitroxides.

Aromatic nitroxides rapidly combine at the nitrogen and oxygen with nitrogen(II) oxide and triphenylmethane to form the corresponding derivatives [139]:



The principal interest lies in the reaction of diphenyl nitroxide with nitrogen dioxide, which leads to the formation of a new free radical, 4,4′-dinitrodiphenylnitroxide [147,176]:

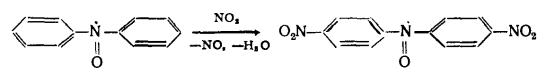
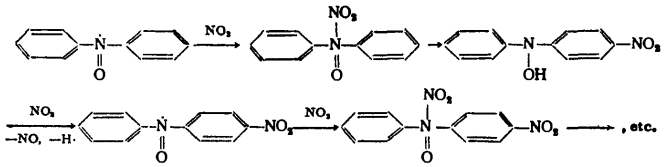
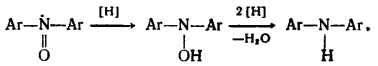


Fig. 3. The EPR spectrum of a benzene solution of diphenyl nitroxide.

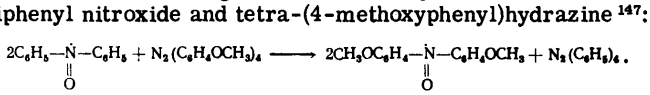
Wieland and Roth[146] demonstrated the complexity of this reaction, which takes place through a series of successive stages‡:



Nitroxides are readily reduced by hydrogen iodide, zinc dust, hydrazine, tin(II) chloride, sulphurous acid, hydrogen sulphide, and hydrogen in the presence of hydrogenation catalysts:



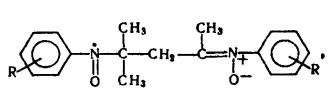
An unusual exchange reaction takes place between diphenyl nitroxide and tetra-(4-methoxyphenyl)hydrazine[147]:



A similar exchange reaction was observed by Möbius and Schneider[177] between 2,2-diphenyl-1-picrylhydrazyl and the peroxide radical[177].

In recent years much attention has been paid to the study of isotropic hyperfine structure parameters of the EPR spectra of diaryl nitroxides. Usually the liquid solutions of these radicals at concentrations $< 10^{-3}$ M show, in addition to the nitrogen triplet, a rich hyperfine structure due to the delocalisation of the unpaired electron at the aromatic nuclei and its reaction with the various *ortho*- and *para*-substituents[157]. For example, the EPR spectrum of bis-(4-methoxy-2,6-dimethylphenyl) nitroxide (Fig. 4) consits of three groups of lines reflecting the interaction of the unpaired electron with the nitrogen nucleus (a_N = = 10 ± 0.3 Oe). Each group has hyperfine structure components with a binomial distribution of intensities due to the splitting of the electronic levels at the 12 protons of the methyl groups and 4 *meta*-protons of the aromatic ring (a_H = 0.8 ± 0.1 Oe). Hence the splitting of the level of the unpaired electron at the methyl groups of the aromatic nuclei serves as a direct experimental proof of the phenomenon of hyperconjugation. Fig. 5 shows the scheme of the interaction of the π-orbital system containing an unpaired electron with the protons of the methyl group.

A special class of aromatic nitroxides is formed by the radicals in which the nitrogen–oxygen group is conjugated with only one aromatic nucleus. A long-known representative of this group is the so-called Banfield and Kenyon's radical, which can be obtained by oxidation of the condensation product of acetone and phenylhydroxylamine[178,179]. Several individual compounds of this class have been described[180,181]:



where R = H, *o*-CH_3, *m*-CH_3, *p*-CH_3, *m*-F, *p*-F, *m*-Cl, *p*-Cl, *m*-Br, *p*-Br, *m*-NO_2.

‡ Analogous reactions can apparently also occur with porphyrexide, mentioned earlier.

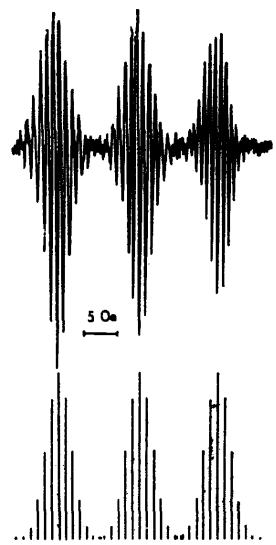


Fig. 4. The EPR spectrum of a benzene solution of bis-(4-methoxy-2,6-dimethylphenyl) nitroxide, with the theoretically calculated spectrum (below).

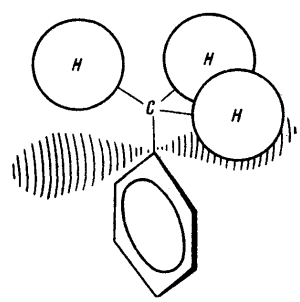
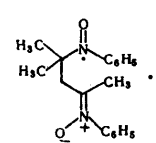


Fig. 5. Scheme of the overlap of the electron clouds of the hydrogen atoms of the methyl group with the π-orbital of the aromatic ring.

The well-resolved EPR spectrum of the Banfield and Kenyon radical was obtained with an oxygen-free tetrahydrofuran solution of the substance. Each of the three quadruplets of the hyperfine spectrum is split into seven lines with a non-binomial distribution of the intensities (Fig. 6).

Detailed analysis of the spectrum showed hyperfine interaction of the unpaired electron with the most removed methyl group, which conformationally can approach closely to the aromatic nucleus containing the unpaired electron[182]:



The other radicals in the series which are known as individual compounds include *trans*-decalyl phenyl nitroxide (I),[183–186] t-butyl 2,6-dimethoxyphenyl nitroxide (II),[141] and 2,6-dimethoxyphenyl 1,1-dimethylbenzyl nitroxide (III).[141] All these substances are obtained by the action

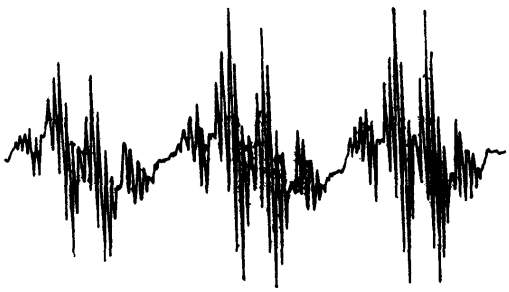
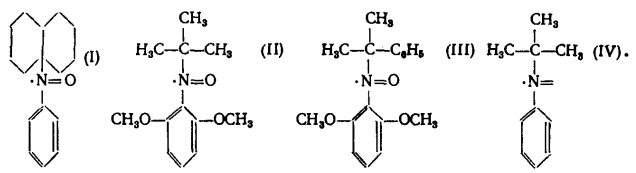


Fig. 6. Hyperfine structure of the EPR spectrum of the tetrahydrofuran solution of the Banfield and Kenyon radical.

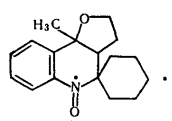
of organometallic compounds on the corresponding nitroso- or nitro-compounds:



(I) m.p. 83°C; (II) m.p. 101–102.5°C; (III) m.p. 77–78°C; (IV) —

Attempts to isolate from solution the individual compound t-butyl phenyl nitroxide (IV) were unsuccessful [141,187,188], despite its obvious structural similarity with (I)–(III).

A large number of aliphatic–aromatic nitroxides is known in solution, but there is not always sufficient basis for ascribing to them a definite structure [189,190]. Many stable nitroxides of the hydrogenated quinoline series were first studied in solution by Razuvaev and coworkers [191,192], but only one individual radical of this class has been obtained pure [193].

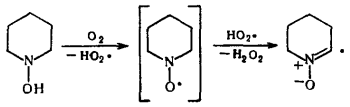


m.p. 101–101.5°C

The hyperfine structure of the EPR spectrum of this radical is a noniplet with ratio of intensities 1 : 2 : 1 : 1 : 2 : : 1 : 1 : 2 : 1, due to the splitting of each component of the nitrogen triplet (a_N = 11.8 Oe) into three lines by the interaction of the unpaired electron with the two protons at positions 6 and 8 of the aromatic ring (a_H = 2.9 Oe).

5. IMINOXYLS

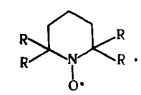
Free iminoxyl radicals§ is the name given to compounds of oxygen(I), which are formed as intermediates in the oxidation of secondary saturated amines [194] and hydroxylamines, for example,



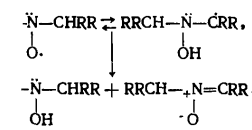
§ This term emphasises the genetic connection of iminoxyls with other radicals of oxygen(I), for example, with hydroxyl (H—O·), alkoxyl (R—O·), and aroxyl (Ar—O·). The terms "amine oxide", "nitroxide", and "aminoxy-radical" are less convenient, as they do not reflect the free-radical nature of these species and contradict the rules for the official nomenclature of organic compounds.

In contrast with the nitroxides it is essential that the NO group of the iminoxyls does not participate in the formation of a conjugated system of multiple bonds, and therefore that the unpaired electron apparently remains localised on the oxygen to a considerable extent.

The existence of free iminoxyls in solutions was first postulated by Rogers and coworkers [195,196]. Rogers assumed that free iminoxyls not possessing α-hydrogen atoms should be stable free radicals. For example, the iminoxyl of piperidine is unstable, but those completely alkylated in positions 2 and 6 of the heterocycle should be stable:

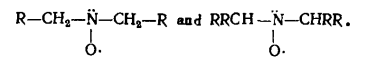


Apparently the substituents R can be not only organic residues, as it is important that the iminoxyls should not be capable of tautomeric conversions of the type:



Lebedev and Kazarnovskii obtained the simplest free radicals of this class by the oxidation of 2,2,6,6-tetramethylpiperidine [197]. The EPR spectrum of this radical in benzene is a triplet with a hyperfine splitting constant of ~ 15.6 Oe [198,199]. Samitov and Lebedev [200] ascribe the anisotropy of the spectrum to contributions from different quantum states in the sublevels of the hyperfine structure and the influence of the quadrupole moment of the nitrogen nucleus [200].

By analysing the parameters $\psi^2(O)$, a_N, and a_H of the EPR spectra of solutions of free iminoxyls in benzene, obtained by oxidising a series of secondary amines and hydroxylamines [201,202], Coppinger and Swalen concluded that the most plausible electronic structure of these radicals corresponds to the formulae:



Hence the valence state of the nitrogen atom, similar to the analogous state of nitrogen in substituted hydroxylamines [66], corresponds to the formula:

$$N[(1s)^2\ (2s+\delta 2p)^2\ (2p+\delta' 2s)^2\ (2p+\delta'' 2s)].$$

The $(2p+\delta' 2s)$ atomic orbitals, being equivalent, should form localised bonding orbitals with the hybrid sp^3-orbitals of the carbon atoms. The $N(2p+\delta'' 2s)$ atomic orbital will overlap with the corresponding orbital of the oxygen atom, forming a third localised orbital.

The EPR spectrum of dialkyliminoxyls in solutions exhibit hyperfine structure due to the interaction of the spin of the unpaired electron with the nuclear spins of the nitrogen atom and the hydrogen atoms adjacent to it (Fig. 7). Table 2 gives the main parameters of the hyperfine structure in the EPR spectra of the free iminoxyls in dilute benzene solutions.

The hyperfine splitting from the nitrogen and hydrogen nuclei is explained by the principal state of the radical's

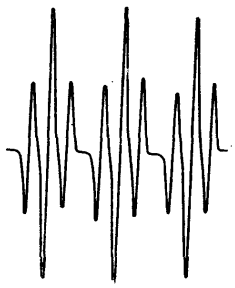
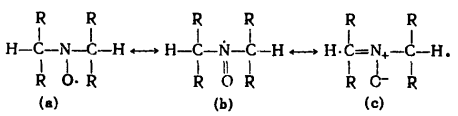


Fig. 7. Hyperfine structure of the EPR spectrum of a benzene solution of di-s--butyl iminoxyl.

TABLE 2. Fundamental parameters of the EPR spectra of free iminoxyls [201].

Formula	a_N	a_H	Number of components	Formula	a_N	a_H	Number of components
$(CH_3CH_2)_2NO$	15.5	10.6	15	$(CH_3CH_2CH)_2NO$	15.4	4.1	9
$(CH_3CH_2CH_2)_2NO$	15.5	10.6	15	CH_3			
$(CH_3CH_2CH_2CH_2)_2NO$	15.7	10.5	15	$(C_6H_5CH_2)_2NO$	15.6	9.5	15
CH_3				$(CH_2{=}CH{-}CH_2)_2NO$	15.5	9.3	15
$(CH_3CH)_2NO$	16.0	4.7	9	$CH_2CH_2CH_2CH_2CH_2NO$	15.4	11.7	15

being capable of representation with the participation of a few valence-isomeric structures [203,204]:



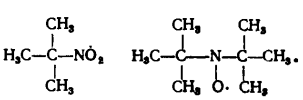
Closely related to the dialkyliminoxyls is a class of labile alkylidene iminoxides of the general formula:

The first radical of this type was observed on subjecting single-crystal dimethyl glyoxime to γ-radiation [205-207].

Many alkylidene iminoxyls were studied in liquid solutions by a flow method [208], using cerium ammonium nitrate [209] and lead tetra-acetate [210] as oxidants.

Most alkylidene iminoxyls are extremely unstable and in the liquid phase many of them have a lifetime measured in fractions of a second, therefore none of the compounds of this class can be obtained in the pure state.

In 1961 Hoffmann and coworkers, using Maki's method [211], observed two EPR spectra (Fig. 8) during the polarographic reduction of 1,1-dimethyl-1-nitroethane, one of these spectra showing the appearance of an unstable anion-radical, and the other belonging to the stable di-t-butyl iminoxyl [212,213]:



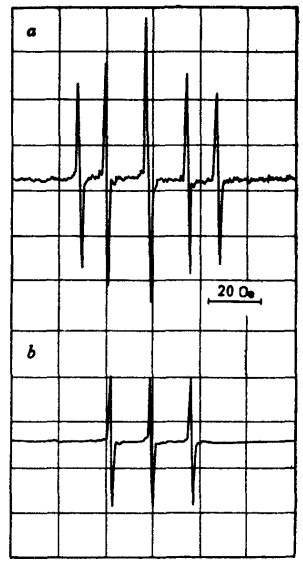


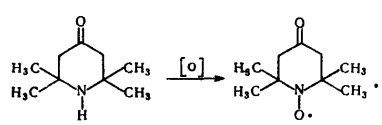
Fig. 8. EPR spectra:
a) mixture of the anion radical of 1,1-dimethyl--1-nitroethane and di-t-butyl iminoxyl; *b*) di-t--butyl iminoxyl (in 1,2-dimethoxyethane).

Di-t-butyl iminoxyl, obtained pure in the reaction of 1,1-dimethyl-1-nitroethane with sodium, is a red liquid, stable in air up to 120°C. [214,215] It is interesting that in the well-resolved hyperfine structure of the EPR spectrum of this radical in addition to three fundamental lines a system doublets — satellites of low intensity — can be observed owing to the interaction of the unpaired electron with the nuclei of the ^{13}C carbon isotope of the methyl groups [216].

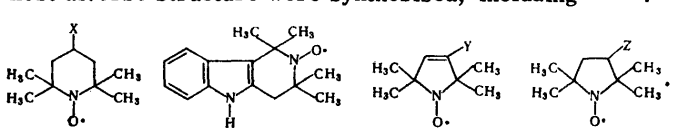
On heating a solution of phorone with a mixture of ammonium nitrate, sodium hydroxide, Trilon B, hydrogen peroxide, and sodium tungstate [217] Razuvaev and coworkers observed that for a few weeks this solution gave a triplet signal which they assumed to belong to a stable radical of triacetonamine formed in the solution [218].

Using preparative thin-layer chromatography on aluminium oxide to separate the paramagnetic mixture, Neiman and coworkers actually separated pure crystalline 2,2,6,6--tetramethyl-4-oxo-piperidine 1-oxide [219].

A new iminoxyl was obtained in high yield by the direct catalytic oxidation of triacetonamine [220]:



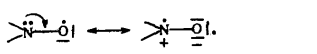
Within a short time many individual iminoxyls of the most diverse structure were synthesised, including [221-225]:



All the free radicals of this series exhibit a singlet when pure, but in solutions they have triplet EPR spectra with a hyperfine splitting constant of ~ 15.5 Oe.

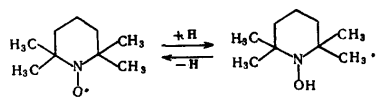
In addition to the ultraviolet, infrared, and EPR spectra, the volatility[226], heat of combustion, and dipole moments of the simplest free iminoxyls have been studied[227].

It is significant that the increase in dipole moment in a free radical, compared with the corresponding hydroxylamine, can in the first approximation be explained by the interaction of the unshared electron pair of the nitrogen atom with the partly free p-orbital atom of the oxygen. Displacement of one of the electrons of the unshared pair of the nitrogen atom to the oxygen atom brings both an increase in the dipole moment of the nitrogen–oxygen bond, and the appearance of spin density at the nitrogen atom:



Comparison of the dipole moments of the radicals and of the corresponding hydroxylamines allowed the distribution of the spin density of the unpaired electron at the N–O bond to be evaluated approximately. The spin density was 27% at the nitrogen atom and 73% at the oxygen atom. Hence the most probable structure of the free iminoxyls is evidently the Coppinger structure[201].

The reduction of free radicals at a mercury dropping electrode[228], hydrogenation[229], and reaction with an alcoholic solution of phenylhydrazine[230] or with an acid solution of a substituted p-phenylenediamine[231] – all these processes lead to the formation of the corresponding substituted hydroxyalamines:

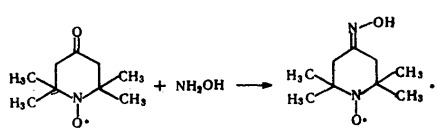


Free iminoxyls readily react with alkyl radicals, which can be used for inhibiting chain radical processes[232–236].

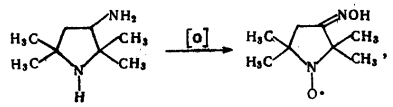
Hence all the free radical reactions of iminoxyls which have been studied proceed exclusively with formation of oxygen derivatives of substituted hydroxylamines, which is also some proof of the predominant localisation of the unpaired electron at the oxygen atom in accordance with the Coppinger structure[201]. However, no proof yet exists that such reactions cannot be accompanied by redistribution of the electron density on the approach of the attacking reagent.

The most notable property of free radicals of this series is their reactions without use of the free valency. This type of reaction can undoubtedly be assumed in various types of chemical and biological systems, especially with high-molecular weight compounds. Nevertheless an unambiguous demonstration that radicals react without participation of the unpaired electron is not available.

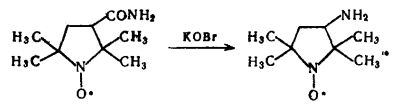
In 1962, Neiman and coworkers first gave an unambiguous proof of the reaction of stable iminoxyls without use of the free valency[237,238], for example¶:



The discovery and organised study of all the possible reactions of iminoxyl radicals without use of the free valency[239–242] defined the limits of its usefulness and this reaction was made a reliable instrument for the synthesis of previously inaccessible free radicals. As an example, it was impossible to obtain an amine radical by oxidising aminopyrrolidine,

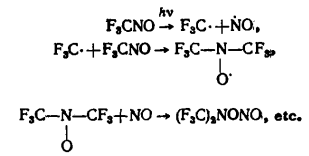


whereas a reaction which did not involve the free valency readily led to the desired product[243]:



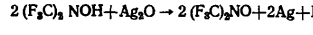
Free iminoxyl radicals very soon acquired great popularity and became the object of steady attention from chemists, physicists, and biologists[244–249].

A study appeared in 1957 which showed that the photochemical decomposition of trifluoronitrosomethane leads to the intermediate formation of bis(trifluoromethyl)-iminoxyl radicals, the existence of which can be judged from their conversion products[250].



Perfluorinated iminoxyl radicals were observed by the EPR method during the polymerisation† of perfluoroethylene in the presence of trifluoronitrosomethane[251] (Fig. 9).

Free bis(trifluoromethyl)nitroxyl was obtained in 1964 by the action of silver oxide on bis(trifluoromethyl)hydroxylamine[253]:



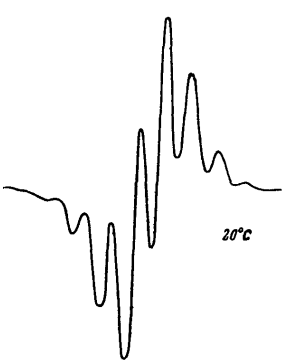


Fig. 9. EPR spectrum of the perfluoroiminoxyl radical.

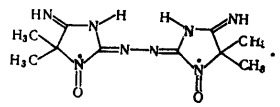
¶ We must remember that Fremy's salt reacts with hydroxylamine by use of the free valency[110].

† Almost simultaneously the hypothesis was propounded that the initiation of the copolymerisation of trifluoronitrosomethane and fluoroalkenes takes place by an anionic mechanism[252].

The same radical was recently obtained pure by a group of Soviet scientists [254,255] who made a detailed study of its properties. It is a violet-pink gas, which readily condenses to a diamagnetic dimer containing ~ 1.5% of the free radical. From the electronic structure of this radical it apparently occupies a position intermediate between the iminoxyls and Fremy's salt.

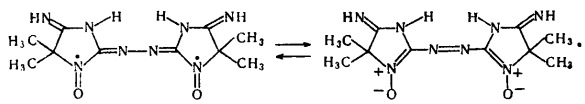
6. INDIVIDUAL POLYRADICALS

As long ago as 1903, Piloty and Vogel, by the reaction of porphyrexide with hydrazine and then with potassium cyanoferrate(III), first obtained a dark blue crystalline compound, which they called porphyrindine [256]:

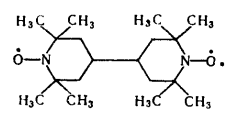


The free-radical nature of this substance was subsequently reliably established by measurement of its magnetic susceptibility [257].

The diamagnetic principal state of porphyrindine is in thermodynamic equilibrium with the excited paramagnetic state which lies only a little higher. This equilibrium shifts in favour of the paramagnetic state on raising the temperature [258]:

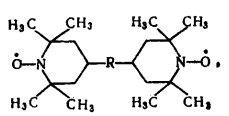


The first representative of the kinetically stable biradicals of the iminoxyl class was obtained during the oxidation of 2,2,2′,2′,6,6,6′,6′,-octamethyl-4,4′-bipiperidyl [259]:



During the study of this substance the discovery was made of the extremely interesting phenomenon of conformational electronic exchange, which is shown in the quintuplet nature of the EPR spectrum (Fig. 10).

To show the mechanism of the interaction of the unpaired electron with the nuclear spins of both nitrogen atoms a series of individual biradicals of diverse chemical structure was synthesised [260]:



where R = OCOO, NHCONH, $OCOC_6H_4COO$, $OCONH[CH_2]_6$. .NHCOO, or $OCO[CH_2]_nCOO$ (n = 0–8). The main method of preparation of the biradicals was by reaction of radicals without use of the free valency. It was found that the effectiveness of the conformational spin–spin interaction is determined not only by the length but also by the flexibility

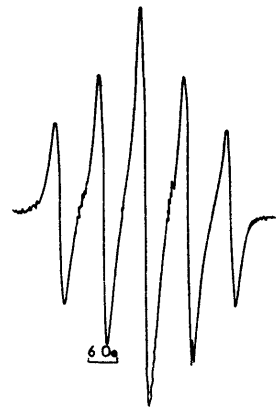
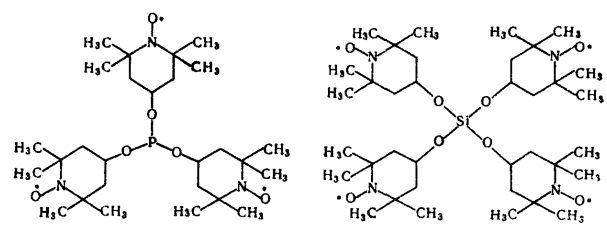


Fig. 10. Hyperfine structure of the EPR spectrum of the first kinetically stable bis--iminoxyl (chloroform solution).

of the bonding chain R, for example, on replacing a polymethylene bridge by p-phenylene, the effect disappeared and the EPR spectrum again became a triplet‡.

A study of free biradicals of the iminoxyl class by the EPR method at different temperatures and in various solvents showed that spin–spin exchange interaction takes place during conformational collisions of two paramagnetic fragments of bis-iminoxyl [266].

A reaction without use of the free valency was successfully used in the syntheses of the first individual free tri- and tetra-radicals of the iminoxyl type [267,268], for example:



The EPR spectra of the triradicals are septets of lines due to the interaction of unpaired electrons with the magnetic moments of three nitrogen nuclei, and for the quadriradicals there are nine components with a separation of ~ 4 Oe between them.

The study of the exchange interaction in polyradicals at different temperatures showed that there is only paired interaction with the neighbouring paramagnetic fragments and during this all the spins of the polyradicals participate in the electronic exchange. In this way instances were first discovered in which the number of unpaired electrons participating in the exchange exceeds two. This brings about the successive transfer of the excitation from one spin to another through the paired collisions. Here we encounter the unusual "memory" of the electron, which is capable of giving information about excitation with a definite rate along the chain of paramagnetic fragments [269].

‡ The EPR spectra of triarymethyl biradicals [261–265] are not significantly different from the analogous spectra of free triarylmethyls.

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REACTIONS OF EPOXYALKANES TAKING PLACE WITH EXPANSION OF THE OXIRAN RING

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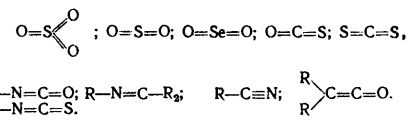
1. INTRODUCTION

Epoxyalkanes are known to be very reactive; their many reactions have been adequately studied and described in the literature [1-4]. Most of the reactions of epoxyalkanes are accompanied by opening of the epoxide ring. Reactions accompanied by enlargement of the ring have been much less studied. The best known among these reactions are the dimerisation of the oxides and the reaction of the oxides with aldehydes and ketones, leading to the production of dioxolans.

The reactions of the oxides with carbon dioxide, leading to cyclic esters of carbonic acid, have also been studied. This process has been carried out on an industrial scale. The alkylene carbonates obtained find application in organic synthesis, as a solvent and for the production of polymers. The methods of making alkylene carbonates, their properties, and applications have been reviewed [5,6].

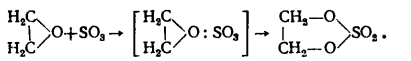
Cyclic products have now been obtained by the reaction of oxides with certain other compounds containing multiple bonds. Such compounds are:



2. REACTIONS WITH SO_3, SO_2, AND SeO_2

The epoxyalkanes react with the anhydrides of some inorganic acids to form cyclic esters.

Thus ethylene sulphate was obtained by the reaction of sulphur trioxide with ethylene oxide in dioxan. It is suggested that initially a coordination compound of sulphur trioxide with ethylene oxide is formed, which then rearranges into the ester [7]:



1,4-Oxathian can be used instead of dioxan [8]. Cyclic alkylene sulphates with 2–6 carbon atoms are obtained by the reaction of corresponding epoxyalkanes with sulphur trioxide in the gas phase at 140°. Sometimes the reagents are diluted with inert gas. 0.1–7.5 moles sulphur trioxide per mole oxide are taken. The cyclic alkylene sulphates formed are removed from the reaction mixture by sublimation [9].

The addition of sulphur dioxide to epoxyalkanes has been studied in greater detail. When sulphur dioxide is passed into ethylene oxide at below 0°, a molecular compound of composition $C_2H_4OSO_2$ is formed [10]. It is used for sterilising soil, as its boiling point is about 20 deg above that of its components.

To obtain ethylene sulphite the reaction is carried out at a higher temperature, either without a catalyst or in the presence of various catalysts. When a catalyst is not used, the ethylene oxide and sulphur dioxide are mixed in the liquid phase and heated under pressure to 140°. The patent states that the reaction is almost complete [11].

Pyridine, amines, amides, phosphines [12], and also quaternary ammonium bases [13,14] have been proposed for use as catalysts in this process.

The polymers of ethylene sulphite formed in the presence of catalysts depolymerise on heating at 140–150°.[13,15] Propylene sulphite can also be obtained by the thermal decomposition of the polysulphite but poly(cyclohex-1,2-ylene sulphite) does not give a monomeric product but forms cyclohexanediol and cyclopentanecarbaldehyde.

The decomposition of polysulphites can also take place under the action of atmospheric oxygen, peroxides, and hydroperoxides, and also under the action of ultraviolet light even at room temperature. By initiating depolymerisation in this way, cyclohex-1,2-ylene sulphite was also obtained from the corresponding polysulphite[16].

The method can be used for making cyclic sulphites which are otherwise unobtainable. For example, 3-hydroxypropylene sulphite, previously unobtainable by other methods, was made by direct reaction of glycidol [2,3-epoxypropan-1-ol (Ed. of Translation)] with sulphur dioxide[14].

To increase the yield of ethylene sulphite, it is recommended that the reaction of ethylene oxide with sulphur dioxide should be carried out in ethylene sulphite or in a mixture of ethylene sulphite and its polymer[17].

Activated carbon, aluminium oxide, zinc chloride, copper(II) chloride, chromium(III) chloride, manganese(II) sulphate, and phosphates at 120–150° can also be used as catalysts for the reaction of ethylene oxide with sulphur dioxide. When active carbon is used (140–160°), dioxan is formed as well as ethylene sulphite (in 1:1 ratio)[18].

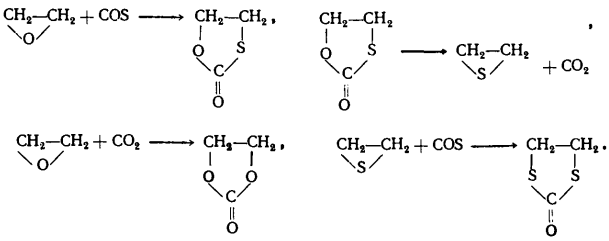
Dioxan is also formed in the thermal decomposition of poly(ethylene sulphite) obtained in the presence of salts of quaternary ammonium bases. Acetaldehyde and water are produced at the same time[14].

Another proposal for making cyclic sulphites is to pass gaseous epoxyalkanes with sulphur dioxide (molar ratio 1:2) under pressure over a catalyst at 200°. The pressure is chosen so that the reaction product is volatilised from the catalyst together with the unreacted reagents. The catalyst can be activated carbon, treated with alkali or silver nitrate and then alkali. Sulphur-resistant catalysts are also used, for example, nickel and/or tungsten sulphides. The cyclic ester is condensed from the effluent gas. Another possibility is to condense the ester product together with the unreacted substances and then separate the mixture by distillation[19]. von Woerden gives other methods of preparing cyclic sulphites and their properties[20].

In the presence of tetraethylammonium bromide, selenium dioxide also adds on to some epoxyalkanes to form cyclic esters of selenous acid[21]. The product of the reaction between selenium dioxide and 1,2-epoxycyclohexane could not be isolated pure. With trimethylene oxide a linear polymeric ester of selenous acid is apparently formed.

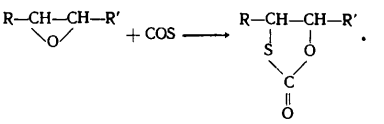
3. REACTIONS WITH CARBONYL SULPHIDE AND CARBON DISULPHIDE

The reactions of the sulphur analogues of carbon dioxide, carbonyl sulphide, and carbon disulphide with epoxyalkanes and the properties of products have been much less studied. At 150° under pressure in the presence of trimethylamine, ethylene oxide and carbonyl sulphide form a copolymer of ethylene *OS*-thiocarbonate and ethylene sulphide[22]; in the presence of tetraethylammonium bromide two products are formed: ethylene carbonate and ethylene *SS*-dithiocarbonate[23,24]. To explain their formation the following scheme has been suggested:



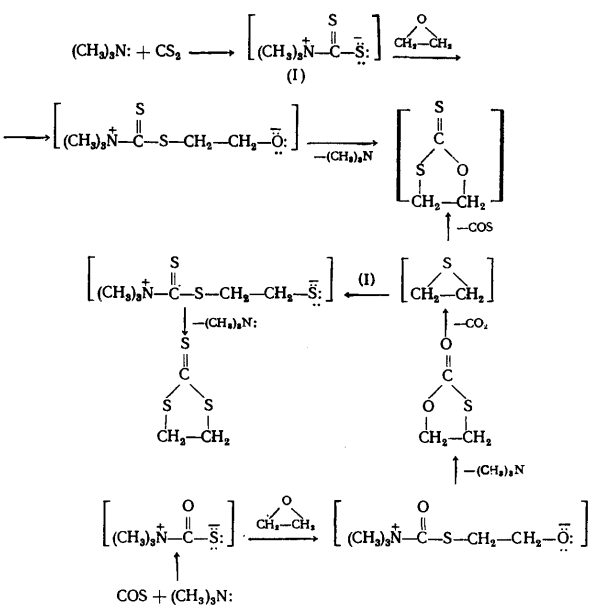
It has been shown that ethylene *OS*-monothiocarbonate in the presence of ethylene oxide and crystalline tetraethylammonium bromide actually decomposes into ethylene sulphide and carbon dioxide at 40–50°.[25]

In the reactions of propylene oxide, 3-chloro-1,2-epoxypropane[23,24], 1-chloro-2,3-epoxybutane, and 1,2-dichloro-3,4-epoxybutane with carbonyl sulphide only one product is formed, by the scheme:



Cyclohex-1,2-ylene oxide and symmetrical oxides such as 2,3-epoxybutane and 1,4-dichloro-2,3-epoxybutane do not react with carbonyl sulphide[26].

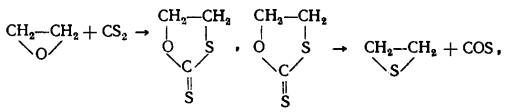
Carbon disulphide also reacts with epoxyalkanes with ring enlargement. In this way Durden and coworkers[27,28] obtained several alkylene trithiocarbonates. The reaction was carried out in the liquid phase under pressure of nitrogen with excess of the epoxyalkane. The maximal yield of ethylene trithiocarbonate was obtained at a carbon disulphide : ethylene oxide molar ratio of 1 : 2.5 and the presence of 0.5 mole % trimethylamine. Carbon dioxide and carbonyl sulphide are formed as side-products, the amount of carbon dioxide formed increasing with decrease in the carbon disulphide : alkene oxide ratio:

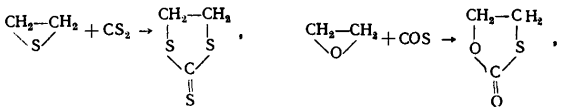


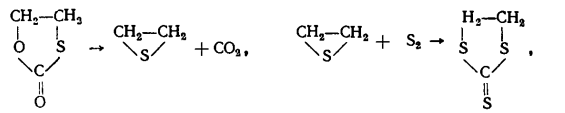
Ethylene sulphide, the intermediate formation of which is postulated in this mechanism, was not isolated from the reaction products.

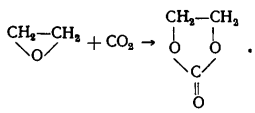
By the same method the authors obtained propylene trithiocarbonate, cyclohex-1,2-ylene trithiocarbonate, phenylethylene trithiocarbonate, and 4-cyanocyclohex-1,2-ylene trithiocarbonate.

The reaction proceeds differently when an equimolar ratio of the reactants is used. Ethylene oxide and carbon disulphide then form a mixture of ethylene trithiocarbonate and ethylene carbonate in the molar ratio 2:1.[29] Their formation can be represented by the scheme:[30]



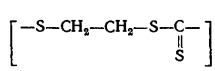




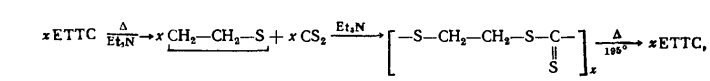


The absence of ethylene dithiocarbonate from the products, although it could be obtained by the reaction of the carbonyl sulphide formed in the process with the ethylene sulphide, suggests that the rate of reaction of the latter with carbon disulphide is much greater than the rate of reaction with carbonyl sulphide.

In connection with the proposed scheme of reaction, the authors made a detailed study of the reaction of ethylene sulphide with carbon disulphide. The reaction proceeded in the presence of triethylamine as catalyst. Temperature was found to greatly affect this reaction. Whereas ethylene trithiocarbonate is the sole product at 100°, at 25° it was accompanied by 37% of a copolymer of ethylene sulphide and carbon disulphide, of composition:



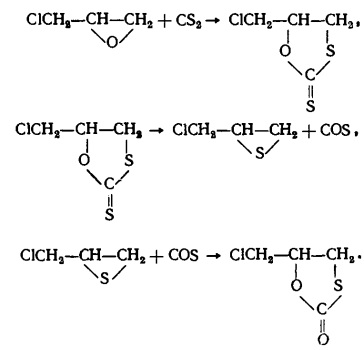
At 195–200° this copolymer decomposes, with formation of ethylene trithiocarbonate. All this can be represented by the scheme[29]:



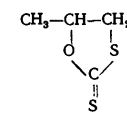
in which ETTC represents ethylene trithiocarbonate.

The decomposition of the ethylene dithiocarbonate obtained initially, which takes place in the presence of hydrogen peroxide and tetraethylammonium bromide, was also confirmed experimentally[31].

3-Chloropropylene *OS*-monothiocarbonate and 3-chloro-1,2-epithiopropane are formed in the reaction of 3-chloro-1,2-epoxypropane with carbon disulphide. Their formation can be represented by the following series of reactions:

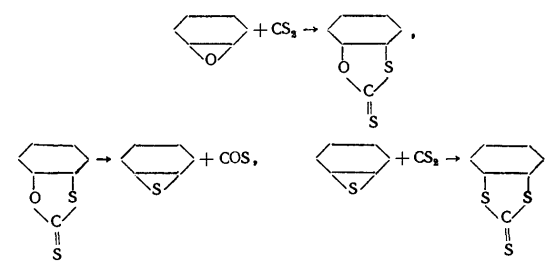


OS-Propylene dithiocarbonate



was obtained as the main product of the reaction of propene with carbonyl sulphide. A little ethylene sulphide was also isolated.

Cyclohex-1,2-ylene trithiocarbonate, a little *OS*-cyclohex-1,2-ylene dithiocarbonate, and carbonyl sulphide are formed in the reaction of 1,2-epoxycyclohexane with carbon disulphide:

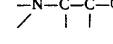


For the reactions of alkylene thiocarbonates see Refs. 32–52.

4. REACTIONS OF EPOXYALKANES WITH ISOCYANATES

Ethylene oxide, propylene oxide, 2-phenyloxiran, and 3-chloro-1,2-epoxypropane bring about the trimerisation of isocyanates. Thus tri(phenyl isocyanate) was obtained by the reaction of ethylene oxide with phenyl isocyanate at room temperature and at 100°.[53] The trimerisation of isocyanates is accelerated in the presence of tertiary amines[54–57].

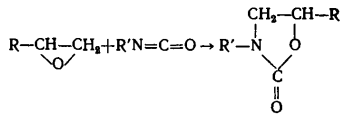
The catalytic action of oxides in the presence of bases is probably due to the formation of the bipolar ion



the existence of which has been shown experimentally[58].

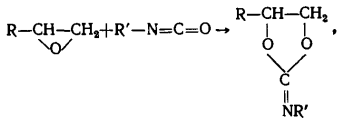
Substituted oxazolid-2-ones were obtained in high yield in the reaction of isocyanates with epoxyalkanes in the presence of tetraethylammonium bromide or potassium iodide

in dioxan, dimethylformamide, or acetonitrile at 150–200°:[54]

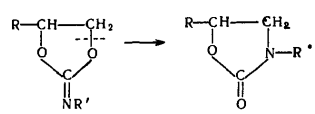


Oxazolid-2-ones were also obtained by the reaction of phenyl isocyanate and epoxides without a solvent at 180–200°.[59–61] Pyridine, tribenzylamine, zinc chloride, lithium chloride, iron(III) chloride, disodium phthalate, alkali, and lead naphthenate act as catalysts for the reaction. Carbonates or sulphites of 1,2-diols, and also cyclic carbonates of α-hydroxy-acids and their sulphite and nitrite analogues[59,61,62], can be used instead of epoxides in the reaction with isocyanates, when they decompose on heating to form the epoxyalkanes. Under the stated conditions, the 3,5-disubstituted oxazolid-2-ones are always formed, as the opening of the epoxide or carbonate ring takes place at the unsubstituted carbon atom[61]. 3-Phenyloxazolid-2-ones were isolated in high yield by the reaction of ethylene carbonate with isocyanate at 130–160° in the presence of *N*-methylmorpholine[63].

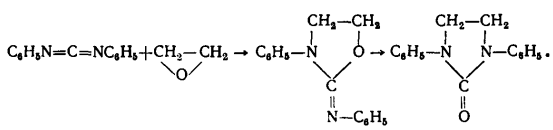
From the above, it follows that reactions between isocyanates and epoxides take place at the N=C bond of the isocyanate. However, Gulbins and Hamann[64,65] showed, by a detailed investigation of this reaction, that the first stage is the addition of the epoxyalkane at the C=O bond of the isocyanate with the intermediate formation of 2-phenylamino-1,3-dioxolane:



which under the conditions of the reaction rearranges into an oxazolid-2-one. This was demonstrated with the aid of a counter-synthesis. 2-Phenylamino-1,3-dioxolan was obtained from phenylimidocarbonyl dichloride and disodium glycollate, and on heating at 200° in the presence of lithium chloride it rearranged to an oxazolidone. A similar reaction takes place at 100° under the action of aluminium chloride[66]. The rearrangement takes place in such a way that the dioxolane ring is broken between the oxygen atom and the unsubstituted CH_2 group:

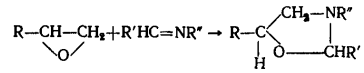


In their structure and reactivity carbodi-imides are reminiscent of isocyanates, therefore their reaction with epoxides or alkylene carbonates in the presence of lithium chloride or pyridine at 200° would be expected to yield substituted imino-oxazolidines. However, instead of these products cyclic ureas, derivatives of imidazolid-2-one, are isolated. As Gulbins and Hamann have shown[65], here initially an imino-oxazolidine is formed, which is converted into 1,3-diphenylimidazolid-2-one by breaking of the C–O bond:



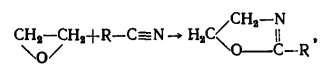
5. REACTIONS OF EPOXYALKANES WITH COMPOUNDS CONTAINING THE GROUPS >C=N–, –C≡N, OR >C=C=O

The reaction of epoxyalkanes with compounds containing >C=N– and –C≡N bonds were investigated by Oda and coworkers[67,68]. Ethylene oxide, propylene oxide, and 3-chloro-1,2-epoxypropane add on to Schiff bases in the presence of tin(IV) chloride (5–10 mole %), to form oxazolidines:



The reactions were carried out in carbon tetrachloride at 10–20°. *N*-t-Butylazomethine reacts with epoxyalkanes with a moderate yield in the absence of catalysts, which can be attributed to its high nucleophilic nature. The use of boron trifluoride as catalyst led to a fall in the yield.

The expected oxazolines



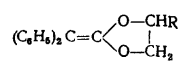
where R = CH_3, $(CH_3)_2CH$, $C_6H_5CH_2$, or CH_2=CH, were isolated from the reaction of epoxyalkanes with nitriles[68].

The reaction was carried out in concentrated sulphuric acid at 5–10°. The existence of side-reactions necessitated the use of a twofold excess of the epoxide, but the yield of the total product was very low (up to 21%). Two isomeric oxazolines were obtained from propylene oxide and acetonitrile. The preferential opening of the epoxide ring at the secondary carbon atom suggests an S_N1 mechanism, which includes the attack of the nitrile on the carbonium ion, and that leads to the opening of the ring of the protonated epoxide.

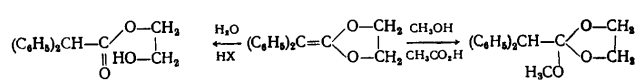
Diphenylacetonitrile reacts with ethylene and propylene oxides in the presence of sodium amide to form imidolactones[65].

In the presence of the >C=C=O system of bonds in ketenes the formation of reaction products with epoxides at both the C=C and the C=O bond can be expected.

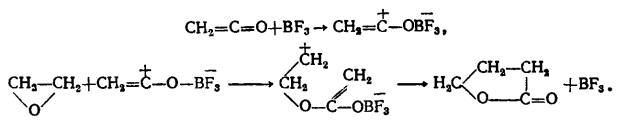
Diphenylketen forms cyclic acetals of diphenylketen on reaction with styrene oxide [phenyloxiran (Ed. of Translation)], γ-phenoxypropylene oxide, ethylene carbonate, and propylene carbonate at 180–200° in the presence of lithium chloride[65]:



The infrared spectra of the compounds obtained show a strong absorption band at 6.05 μm (1653 cm^{-1}) due to the C=C double bond; the absorption band of the carbonyl group was not observed. The structure of the acetals was confirmed by the formation of the ortho-ester of diphenylacetic acid on reaction of the acetal from diphenylketen and ethylene oxide with methanol in the presence of acetic acid, and also by the formation of 2-hydroxyethyl diphenylacetate on hydrolysis:



Hence it was shown that diphenylketen reacts with epoxides at the C=O bond. The rearrangement of the acetal into a γ-lactone was not observed. In contrast to this, Oda and coworkers[70] showed that aliphatic and aromatic α-oxides react with keten in the presence of boron trifluoride–diethyl ether at the C=C bond to form γ-lactones:

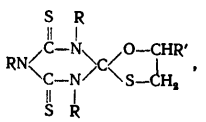


Lactones are obtained in ~ 10% yield on passing keten into an ethereal solution of an epoxide in the presence of 5 mole % boron trifluoride–diethyl ether at 5–50°. In this way, ethylene oxide, 1,2-epoxypropane, styrene oxide, and 3-chloro-1,2-epoxypropane gave respectively γ-butyrolactone, γ-valerolactone, γ-phenyl-γ-butyrolactone, and γ-chloromethyl-γ-butyrolactone.

6. REACTIONS OF EPOXYALKANES WITH ISOTHIOCYANATES

The reaction of epoxyalkanes with the nearest sulphur analogues of the isocyanates — the isothiocyanates — is quite unique.

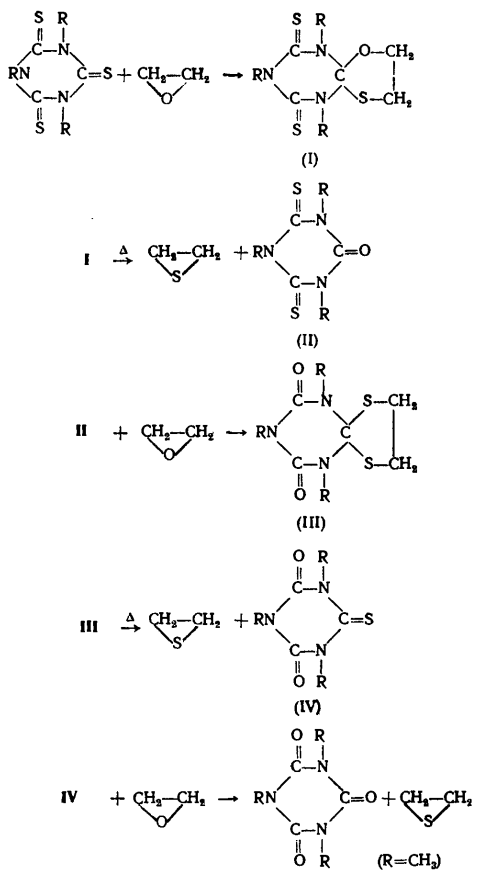
The simplest isothiocyanate, methyl isothiocyanate, reacts with ethylene oxide in the presence of tetraethylammonium bromide to form hexahydro-1,3,5-trimethyltriazine-2,6-dithione-4-spiro-2′-(1,3-oxathiolan):[71]



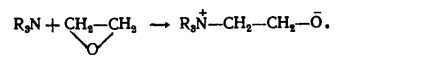
where R = CH_3 and R′ = H.

When this compound is heated to 200° in dioxan it decomposes with liberation of ethylene sulphide and trimethyl dithioisocyanurate; oxidation of it with nitric acid led to trimethyl isocyanurate. It was shown that the formation of a spiro-compound proceeds through the formation of the trimethyl ester of trithioisocyanuric acid, which then reacts at the C=S bond with the ethylene oxide[72]. Trimethyl trithioisocyanurate was obtained by trimerisation of methyl isothiocyanate in a solution of the oxides in the presence of catalytic amounts of triethylamine or pyridine, An analogous reaction also takes place in a solution of triethylamine in the presence of catalytic amounts of epoxyalkanes, that is, the latter in conjunction with tertiary amines bring about trimerisation of the methyl isothiocyanate. The reaction does not take place in the absence of the oxides.

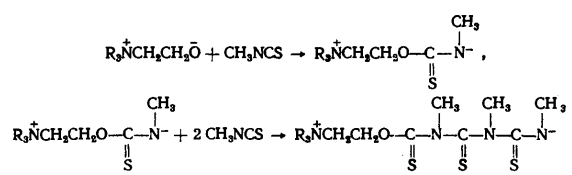
The liberated trimethyltrithioisocyanurate reacts with ethylene oxide, propylene oxide, and 3-chloro-1,2-epoxypropane in the presence of tetraethylammonium bromide to form the corresponding spiro-compounds, which when heated to 200° decompose into alkylene sulphide and trimethyl dithioisocyanurate[72]. On the reaction of propylene oxide with methyl isothiocyanate, the trimer of methyl isothiocyanate is obtained in addition to the spiro-compound; increasing the duration of the reaction leads to the production of only one spiro-compound[72]. This once again confirms that in the reactions with epoxyalkanes the methyl isothiocyanate is first trimerised and then the trimer reacts with the alkylene oxide at the C=S bond. The decomposition product of the spiro-compounds, trimethyl dithioisocyanurate, also reacts with ethylene oxide at the C=S bond to form a new spiro-compound which when heated to 200° liberates ethylene sulphide and trimethyl monothioisocyanurate. The latter reacts with ethylene oxide to give first a spiro-compound and then trimethyl isocyanurate. Hence, on starting from trimethyl trithioisocyanurate, trimethyl isocyanurate was obtained, that is, complete replacement of sulphur by oxygen took place under the action of ethylene oxide[72]:

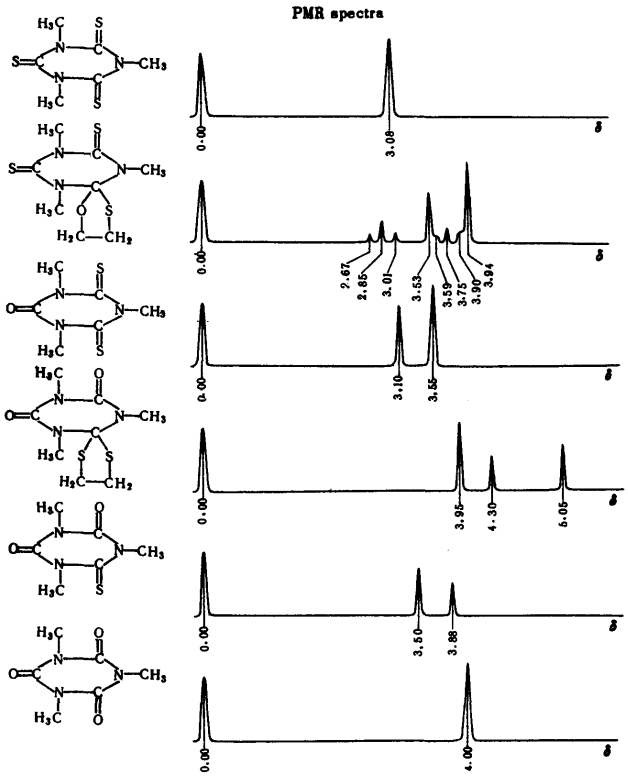


The structure of all the compounds obtained was confirmed by use of PMR spectroscopy (Figure).[73] It can be assumed that the mechanism of formation of trimethyl trithioisocyanurate and the spiro-compound is analogous to the reaction of the trimerisation of isocyanates. A bipolar ion acts as catalyst[58]:

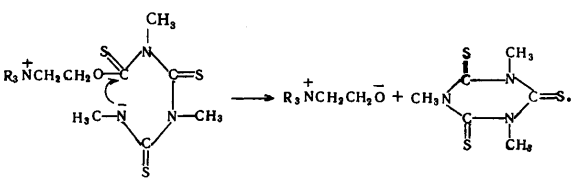


The ion formed adds on to the N=C bond of the isothiocyanate to form a nitrogen anion, which continues the chain growth up to the stage of the trimer:

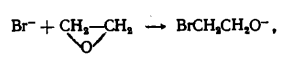




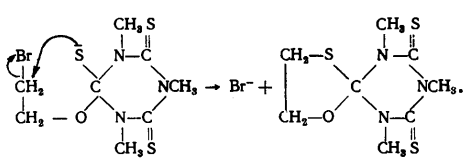
Then the ring closes with release of the original catalyst:



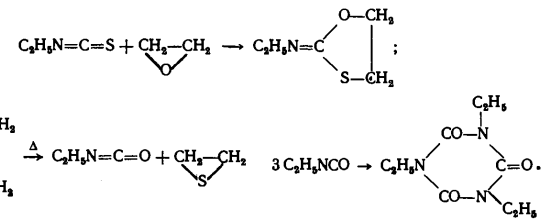
In the presence of tetraethylammonium bromide the anion acts as catalyst:



which catalyses the trimerisation of methyl isothiocyanate. The trimethyl trithioisocyanurate obtained is attacked by the anion at the C=S bond, leading to an anion with a negative charge at the sulphur atom, which closes into a ring by displacing a bromide anion:

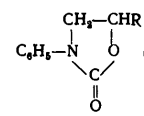


The nearest homologue of methyl isothiocyanate, ethyl isothiocyanate, reacts with ethylene oxide in the presence of tetraethylammonium bromide somewhat differently. In addition to the spiro-compound, triethyl isocyanurate [75] and ethylene sulphide were isolated from the reaction mass; their formation can be represented as follows:

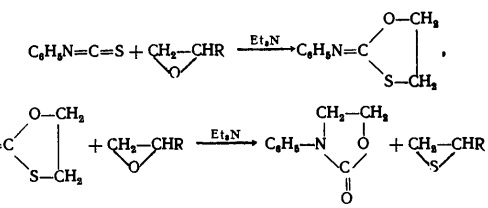


Epoxyalkanes in conjunction with basic compounds are known to bring about trimerisation of isocyanates [54]. Here the trimerisation proceeds under the influence of the sulphur analogue of ethylene oxide — ethylene sulphide — and traces of triethylamine.

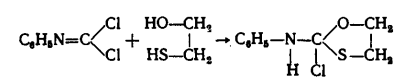
Phenyl isothiocyanate reacts with epoxyalkanes in the presence of triethylamine to form compounds which do not contain sulphur — 3-phenyloxazolid-2-ones [74]:



where R = H, CH_3, or CH_2Cl. The scheme for obtaining oxazolid-2-ones can be represented as follows:



The 2-phenylimino-1-thio-3-oxolan which is formed as an intermediate readily reacts with the epoxyalkane giving an oxazolidone and the corresponding epithioalkane. The possibility of such a reaction taking place is confirmed by the fact that 2-phenylimino-1-thio-3-oxolan is formed from phenylimidocarbonyl dichloride and mercaptoethanol in the presence of triethylamine [75]; ethylene oxide converts the product into 3-phenyloxazolid-2-one. On using pyridine as an acceptor for the hydrogen chloride the above reaction between phenylimidocarbonyl dichloride and mercaptoethanol leads to the production of 2-chloro-2-phenylamino-1-thio--3-oxolan:



which also reacts with ethylene oxide, to form 3-phenyloxazolid-2-one [76]. The reaction probably takes place through the stage of formation of 2-phenylimino-1-thio--3-oxolan.

Hence in the reaction of epoxyalkanes with isothiocyanates, the epoxide opens the C=S bond in the N=C=S system of double bonds.

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INTERMOLECULAR ENERGY TRANSFER IN PHOTOCHEMICAL REACTIONS IN SOLUTIONS OF ORGANIC COMPOUNDS†

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1. INTRODUCTION

When a molecule of an organic compound absorbs a quantum of light, it undergoes transition from the ground electronic state to an excited state. The nature of the electronic transitions in the molecule may be explained by means of the somewhat modified Jablonski diagram shown in Fig. 1.[2] For most compounds the ground state of the molecule S_0 is the singlet state, in which the total spin of the orbital electrons (s) is equal to zero, and the multiplicity, denoted by the quantity $2s + 1$, is unity. Electronic transitions from S_0 to excited singlet levels S_1, S_2, etc., without change of spin orientation, are much more probable than transitions with change in multiplicity; generally speaking, the latter are forbidden. According to present interpretations[3], a molecule at a high excited singlet level, S_2, S_3 etc., passes to a lower S_1 level in $\sim 10^{-13}$ s without emission of radiation, where it remains for 10^{-7}–10^{-9} s. The molecule may pass from the S_1 level to the S_0 ground level either without or with the emission of light (fluorescence).

The molecule may also pass from the excited singlet level to a lower triplet level T, for which the resultant spin of the electrons is unity, and the multiplicity is 3.[4,5] A transition from the triplet level to the ground state with a change in multiplicity is forbidden; the molecule therefore remains in the triplet state much longer than in the singlet excited state. A spontaneous transition from the triplet to the ground state may be accompanied by the emission of light (phosphorescence). Compared with fluorescence, phosphorescence is marked by a longer decay period (up to several seconds) and by a displacement towards the long-wave region of the spectrum.

The excited molecules may undergo various unimolecular chemical conversions or enter into chemical reactions with other molecules.

† A previous review dealt with intermolecular energy transfer in the radiolysis of solutions of organic compounds[1].

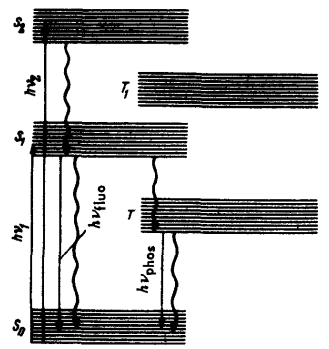


Fig. 1. Scheme of electronic transitions in an organic molecule. The straight arrows correspond to transitions with absorption or radiation of light. The wavy arrows correspond to transitions without radiation.

In multicomponent systems the excited molecules of one component may transfer energy to molecules of another component. The special features of intermolecular energy transfer are largely due to the large number of the excited molecules that take part in it. Energy transfer may occur at singlet levels:

$$A^{S_1} + B^{S_0} \rightarrow A^{S_0} + B^{S_1}.$$

A^{S_1} and B^{S_1} are excited singlet molecules of the energy donor and acceptor, A^{S_0} and B^{S_0} are donor and acceptor molecules at the ground singlet level. This process is called singlet-singlet energy transfer.

If the energy is transferred from the triplet level of the molecule A to the molecule B according to the scheme:

$$A^{T} + B^{S_0} \rightarrow A^{S_0} + B^{T},$$

the process is called energy transfer at triplet levels or triplet-triplet transfer.

The molecules B^{S_1} and B^{T} formed as a result of energy transfer may be deactivated with the emission of luminescent light. This phenomenon is called sensitized fluorescence or sensitized phosphorescence. If the molecules of A are also capable of showing luminescence, quenching of the glow due to the energy of the donor will also be observed.

As a result of energy transfer, chemical conversion of the acceptor may be sensitized or the photochemical reaction of the donor may be inhibited.

It is generally considered that for energy transfer to occur, the level of the excited donor molecule, from which transfer takes place, should be higher than the excited level of the acceptor molecule.

The transfer of energy between singlet levels in solution may occur not only at a direct diffusion approach of the interacting molecules, but also at distances greatly exceeding the kinetic radii of the molecules. In the latter case, the greater the overlap of the fluorescence spectrum of the donor and the absorption spectrum of the acceptor, the greater will be the effectiveness of the transfer. Förster[6] and Galanin and Frank[7] explained the phenomenon of long-range action in singlet-singlet energy transfer in solution by dipole-dipole interactions of the excited donor molecule with the acceptor molecule. These authors

showed that the probability of the "resonance" transfer of energy (W) is determined by the expression:

$$W = \frac{1}{\tau}\left(\frac{R_0}{R}\right)^6,$$

where τ is the lifetime of the excited energy-donor molecules, R is the distance between the interacting molecules, and R_0 is the so-called critical radius of resonance interaction, which is determined by the optical properties of the system, particularly by the oscillator strengths and the area of overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor.

The transfer of energy at triplet levels was first observed by Terenin and Ermolaev[8] in investigating the phosphorescence of a solid solution of naphthalene sensitized with benzaldehyde or benzophenone under the action of light of wavelength 365 nm absorbed by the donor molecules (naphthalene is virtually transparent in this spectral region). The triplet level of naphthalene is lower, and the singlet level higher, than the corresponding levels of benzaldehyde and benzophenone. In this connection the transfer of energy to naphthalene can only take place at the triplet levels.

In liquid solutions, triplet-triplet energy transfer was first discovered by Bäckström and Sandros[9], who studied the quenching of biacetyl phosphorescence by aromatic compounds with triplet levels lower than the triplet level of biacetyl. These workers showed that the rate of energy transfer at triplet levels is close to the value determined by the rate of diffusional encounter of the interacting molecules.

Aromatic compounds containing carbonyl groups are frequently used as energy donors in triplet-triplet transfer[10]. This is because these compounds have high triplet levels and low singlet levels. Moreover, when electronically excited, these compounds show a high probability (frequently close to unity[11,12]) of passing to the triplet state because of the strong spin-orbital interaction in $n \rightarrow \pi^*$ transitions[3].

The most reliable results on triplet-triplet energy transfer in liquid solutions have been obtained by Porter and Wilkinson[13] by the method of flash photolysis. Essentially, this method consists in producing a high concentration of intermediate particles — radicals or triplet molecules — in solution by means of short-duration light impulses of high intensity; the optical absorption of these particles is determined by means of a "sounding" beam. Flash photolysis may be used to determine both the absorption spectrum of the intermediate particles and the change in their concentration with time.

Using this method, Porter and Wilkinson were able to follow the change in the rate of disappearance of the triplet states of a number of aromatic compounds (energy donors) in the presence of acceptor additives. In some instances they were also able to observe triplet acceptor molecules that arose as a result of energy transfer. The absolute rates of triplet-triplet energy transfer were determined and were found to be close to the diffusion rates, in agreement with the results of Bäckström and Sandros[9].

At present, the mechanism of energy transfer at triplet levels is not quite clear. Terenin and Ermolaev[14,15] consider that the transfer proceeds by an exchange-resonance mechanism[16]. This mechanism requires overlapping of the electronic shells of the interacting molecules, which is in agreement with the diffusion mechanism of energy transfer in solutions.

At low acceptor concentrations, the intermolecular energy transfer competes with the spontaneous deactivation of the excited donor molecules. If the energy transfer is regarded as a bimolecular process, the dependence of the quantum yield on the acceptor concentration can be expressed by simple equations. For the quantum yield (γ) of sensitized processes (luminescence or chemical decomposition) the equation has the form:

$$\frac{\gamma}{\gamma_{lim}} = \frac{k_{AB}\tau\,[B]}{1 + k_{AB}\tau\,[B]}, \qquad (1)$$

where γ_{lim} is the limiting quantum yield of the sensitized process at sufficiently high concentrations of B, when there is no spontaneous deactivation of the excited molecules of A; k_{AB} is the rate constant for energy transfer; and τ is the lifetime of excited molecules of A.

If the acceptor is a quencher, the quantum yield for luminescence or chemical decomposition of the donor is determined by the Stern–Volmer equation:

$$\frac{\gamma}{\gamma_0} = \frac{1}{1 + k_{AB}\tau\,[B]}, \qquad (2)$$

where γ_0 is the quantum yield in the absence of quencher.

Although these equations have been derived from the simplest kinetic considerations and are semiempirical, in many instances they are nevertheless in good agreement with experimental results. The product $k_{AB}\tau$, which is determined from the dependence of the quantum yield on the concentration of B, is a measure of the effectiveness of the transfer of excitation energy.

The information presented in this section is sufficient for an understanding of the material on specific photochemical reactions discussed below. Detailed analyses of the problem of intermolecular energy transfer during luminescence may be found in a number of publications[10,17–22].

In the present review, problems of energy migration in biologically important systems[19–23] are not considered, nor are papers on the migration of energy in photochemical reactions in the gas phase and in solid and vitreous media.

The data in a number of papers considered in the review do not allow an unambiguous conclusion to be drawn as to the mechanism of energy transfer; for this reason, it would obviously not be expedient to classify the material on the basis of transfer mechanism. It is arranged according to the type of chemical reaction accompanying the energy transfer.

2. SENSITIZED PHOTODECOMPOSITION

a. Halogeno-Substituted Hydrocarbons

One of the first papers on sensitized photolysis of organic compounds was that of West and Paul[24], published in 1932; they studied the photolysis of solutions of ethyl iodide in hexane and benzene under the action of light of wavelength 254–280 nm (maximum radiation in 261 nm region). Unlike hexane, benzene is not transparent in the 261 nm region, and a considerable portion of the light is absorbed by the solvent in benzene solutions. In particular, with a solution of concentration 0.03 M, benzene absorbs 180 times as much light as ethyl iodide. However, the quantum yield for the photodecomposition of ethyl iodide in such a solution is virtually the same as that for

the photolysis of a 0.03 M solution in hexane, in which light is only absorbed by the ethyl iodide. To explain these results, the authors suggested that excited benzene molecules may transfer energy to ethyl iodide molecules, which decompose into free radicals.

Later, West and Fitelson[25] showed that the sensitized decomposition of ethyl iodide may also occur in such solvents as methyl iodide, hydrogen sulphide, and chlorobenzene, the first two solvents themselves decomposing under the action of light. The transfer of energy to ethyl iodide appears to compete with the decomposition of excited molecules of these solvents.

To explain the mechanism of energy transfer in these reactions, West and Miller[26] compared the kinetics of the naphthalene-sensitized photodecomposition of ethyl iodide in hexane with the kinetics of the quenching of naphthalene fluorescence.

The rate of decomposition of ethyl iodide under the action of light of wavelength 313 nm, which only excites naphthalene, is proportional to the amount of light absorbed. The additivity of the spectral changes that occur when solutions of naphthalene and ethyl iodide are mixed clearly indicates that there is no appreciable complex formation in the unexcited state. Thus, the decomposition of ethyl iodide is the result of transfer of excitation energy. With an ethyl iodide concentration of less than 0.01 M, the quantum yield of the decomposition obeys Eqn. (1); $\gamma_{lim} = 0.3$ agrees with the quantum yield for the decomposition that occurs when light acts directly on ethyl iodide, that is, all the light energy absorbed by naphthalene is transferred to the ethyl iodide. Under these conditions $k_{AB}\tau \simeq 10^3$ litre mole^{-1}.

The quenching of naphthalene fluorescence by ethyl iodide follows the Stern–Volmer law. However, here $k_{AB}\tau = 180$ litre mole^{-1}. The authors explain the difference in the effectiveness of energy transfer obtained from data on fluorescence and data on photolysis on the assumption that the photodecomposition of ethyl iodide is brought about by the transfer of energy, not only from the fluorescing level of the naphthalene molecule, but also from the excited level from which the molecule does not fluoresce. This is probably a triplet level, although the authors themselves put forward no suggestions as to its nature. This is due to the fact that the paper by West and Miller appeared before Terenin[4], and then Lewis and Kasha[5], developed an interpretation of the triplet excitation levels and their roles in photochemical reactions.

Ethyl iodide weakly absorbs light of wavelength 313 nm; for this reason, only ethyl iodide molecules at high vibrational levels absorb light of this wavelength and pass to the excited electronic state, which here is a repulsive state.

However, in the presence of naphthalene and with ethyl iodide concentrations greater than 0.01 M, all the energy of light of wavelength 313 nm absorbed by naphthalene is transferred by ethyl iodide molecules. Evidently, ethyl iodide molecules in the lower vibrational levels can receive energy quanta from naphthalene molecules of a size such that they would remain virtually unabsorbed under the direct action of light. The explanation of this effect given by West and Miller is illustrated schematically in Fig. 2. Curve *1* is the potential curve of ethyl iodide in the ground state; the shape of the curve should not change appreciably in collisions between unexcited molecules of naphthalene (N) and ethyl iodide (Et–I), since there is little interaction between these; *2* is the repulsion curve of ethyl iodide. The energy of the configuration formed when a molecule of

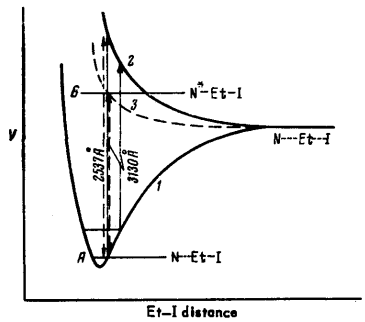


Fig. 2. Mechanism of photosensitized decomposition of ethyl iodide.

ethyl iodide collides with an excited naphthalene molecule (curve *3*) will be less than the energy of (EtI)*, if there is appreciable interaction between the excited naphthalene molecules (N*) and ethyl iodide. Accordingly, the sensitized decomposition of ethyl iodide requires less energy than that required under the direct action of light.

Wilkinson[27] studied the sensitized photodecomposition of solutions of 1-iodonaphthalene in the presence of various sensitizers under the action of light of wavelength 365 nm, for which iodonaphthalene is virtually transparent. The photodecomposition of iodonaphthalene occurs in the presence of additives (acetophenone, benzophenone, anthraquinone, 2-acetonaphthone), the triplet level of which lies above the corresponding naphthalene level, and it does not occur when the triplet level of the additive (anthracene) is lower than that of iodonaphthalene. The reaction probably proceeds by the transfer of energy between the triplet levels.

Kallmann-Oster and Kallmann[28], who studied the concentration dependence of free radical yields in the photolysis and radiolysis of carbon tetrachloride solutions in benzene, concluded that the sensitized photodecomposition of carbon tetrachloride is the result of transfer of energy from benzene to CCl_4‡. The rate of formation of free radicals was determined with the aid of the free-radical acceptor 1,1-diphenyl-2-picrylhydrazyl (DPPH). The concentrations of DPPH and CCl_4 were such that the direct action of light ($\lambda = 254$ nm) on these compounds could be neglected. The rate of formation of free radicals in photolysis reaches a limiting value at CCl_4 concentrations of about 10^{-2} M, and it decreases in the presence of additions of the organic luminophores, fluoranthene, *p*-terphenyl, and phenylbiphenylyloxadiazole. The authors consider that energy transfer occurs at low excited singlet levels. Van Dusen and Hamill[29], who studied the photolysis ($\lambda = 254$ nm) of mixtures of benzene with carbon tetrachloride, ethyl iodide, chloroform, and other chlorides over a wide concentration range, consider that sensitized photodecomposition of chlorides is associated with transfer of energy from benzene at the triplet levels.

Semeluk and Unger[30], who studied the benzene-sensitized photodecomposition of chloroform in the gas phase,

‡ We have already discussed in detail the problem of energy transfer in the radiolysis of solutions containing CCl_4 and other halogeno-substituted hydrocarbons[1]. See also Van Dusen and Hamill[29].

also consider that decomposition of chloroform is due to triplet-triplet energy transfer from benzene to chloroform.

When the sensitizing additive itself undergoes chemical change, it is difficult to decide whether the photochemical reaction is due to the transfer of energy from this additive and subsequent reaction of acceptor decomposition products with the additive, or to the immediate entry of excited additive molecules into photochemical reaction with the other compound. Thus, Bowen and Rohatgi[31] found that when light acts on anthracene (A) dissolved in carbon tetrachloride, recombination products of $^{\cdot}ACl_4$ and $^{\cdot}CCl_3$ radicals are formed. They consider that the latter radicals are formed by abstraction of a Cl$^{\cdot}$ atom from CCl_4 by excited anthracene.

To find the nature of the excited anthracene molecules which react with carbon tetrachloride, Kusuhara and Hardwick[32] compared the rate of this reaction for anthracene under the direct action of light with that for anthracene excited by energy transfer from coronene. It was first shown by flash photolysis that energy is transferred from coronene to anthracene at triplet levels. The relative concentrations of triplet molecules produced by direct action and as a result of energy transfer were also evaluated. Comparison showed that the rates of the direct and sensitized reactions are proportional to the concentrations of triplet anthracene molecules. Bagdasar'yan[33,34] observed an increase in the rate of initiation of photopolymerization of various vinyl monomers (styrene, α-methylstyrene, allyl acetate, isoprene, chloroprene) in the presence of CCl_4; he considers this to be due to the removal of Cl$^{\cdot}$ atoms from CCl_4 by excited monomer molecules. Robb and coworkers obtained analogous results in a study of the photochemical telomerization of styrene and methyl methacrylate with CCl_3Br.[35,36]

b. Some Other Readily Decomposable Compounds

Organic peroxides, hydroperoxides, azo- and diazo-compounds, disulphides, and some other compounds are readily decomposed in solution under the action of light, and some are also decomposed by heating; for this reason, they are frequently used as sources of free radicals in the initiation of chemical reactions[37,38]. Because of the readiness with which these compounds are decomposed when electronically excited, they may be used as very sensitive acceptors in sensitized reactions.

Luner and Szwarc irradiated dilute benzene solutions of acetyl peroxide with light of wavelength 254 nm, which is absorbed virtually by benzene alone, and they observed sensitized decomposition of the peroxide[39]. Sensitized decomposition of the peroxide also occurs in iso-octane in the presence of anthracene or naphthacene under the action of light of wavelength 265 nm, which is absorbed by these hydrocarbons.

Krongauz and Bagdasar'yan[40], and later Vasil'ev and Krongauz[41,42], made a detailed study of the solvent-sensitized radiolysis and photolysis of benzoyl peroxide in benzene and in toluene. Luminophore additives (anthracene, phenanthrene, *p*-terphenyl, etc.) reduce the yield in the sensitized decomposition of benzoyl peroxide. At the same time, benzoyl peroxide quenches the solvent-sensitized fluorescence of these luminophores. They suggested that the same excited states of the solvent molecules participate in the transfer of energy both to the peroxide and to the luminophore, and they obtained concordant values of the constants for energy transfer from the solvent to the additives; these values were calculated from data on the sensitized fluorescence of the luminophores and the sensitized decomposition of peroxide in three-component solutions (solvent–benzoyl peroxide–luminophore). In sensitized fluorescence, the energy transfer occurs at singlet excitation levels. Thus, the decomposition of benzoyl peroxide also appears to be due to singlet-singlet energy transfer. Subsequently, an attempt was made to give a more detailed elucidation of the mechanism of energy transfer in these systems[43-45]. It was shown that energy transfer occurs at a distance exceeding the kinetic radii of the molecules, but the effectiveness of the transfer largely depends on the rate of diffusion of the molecules in the solution.

The sensitized photodecomposition of benzoyl peroxide resulting from the transfer of energy from the luminophores to the peroxide has also been studied. This process leads to quenching of the luminophore phosphorescence, which also indicates singlet-singlet energy transfer. However, here the rate constant for the transfer is much lower than with sensitization by a solvent and it is in satisfactory agreement with the hypothesis that energy is transferred by diffusion approach of the molecules to a distance equal to the kinetic radii.

Kardash and Krongauz[46] compared the kinetics of the naphthalene-sensitized photodecomposition of propionyl peroxide in benzene under the action of light of wavelength 313 nm (which is absorbed only by naphthalene) with the kinetics of the photolysis of solutions of naphthylpropionyl peroxide; they showed that naphthylpropionyl peroxide decomposes by a bimolecular mechanism. With peroxide concentrations less than 5×10^{-3} M, the quantum yield tends to zero. In the low-concentration region, the concentration dependence of the quantum yield for the photodecomposition of naphthylpropionyl peroxide is similar to the same dependence for a 2:1 mixture of naphthalene and propionyl peroxide. It appears that excited molecules of naphthylpropionyl peroxide can transfer energy directly to the peroxide groups of other molecules.

Überreiter and Bruns[47] studied the fluorenone-sensitized photodecomposition of tetralin hydroperoxide in chlorobenzene under the action of light of wavelength greater than 365 nm. At concentrations less than 5×10^{-3} M, the rate of decomposition of tetralin hydroperoxide is proportional to the hydroperoxide concentration. The sensitized decomposition of the hydroperoxide is due to energy transfer between triplet levels; the formation of hydrogen bonds between the donor and acceptor plays an important part in this transfer. The authors consider that this is confirmed by the failure of fluorenone to sensitize the photodecomposition of benzoyl peroxide, with which it does not form hydrogen bonds. The rate of hydroperoxide photodecomposition depends linearly on the square root of the fluorenone concentration; this appears to be related to the mutual deactivation of two triplet fluorenone molecules.

In a study of the so-called "delayed fluorescence" of a number of aromatic luminophores in solution, Parker and Hatchard observed similar interaction between two triplet molecules with the formation of excited and unexcited singlet molecules[48]:

$$A^T + A^T \longrightarrow A^{S_1} + A^{S_0}.$$

The benzophenone-sensitized photodecomposition of diazomethane into methylene and nitrogen is an interesting example of a reaction resulting from energy transfer at

triplet levels. When light acts directly on diazomethane[49,50] dissolved in cyclohexene, or when diazomethane is decomposed by heat, a mixture of norcarane and methylcyclohexenes is formed, as a result of the reaction of cyclohexene with methylene, which appears to occur in the singlet state. In the photodecomposition of diazomethane sensitized by benzophenone (as noted above, on photoexcitation benzophenone passes virtually completely into the triplet state), norcarane is mainly formed. This appears to be related to the triplet state of the methylene in this case. Methylene formed by the direct photolysis of diazomethane in octane reacts with *cis*- or *trans*-but-2-ene to give the corresponding *cis*- or *trans*-dimethylcyclopropane. At the same time, when diazomethane undergoes sensitized photodecomposition, a mixture of *cis*- and *trans*-dimethylcyclopropane is always formed. The intermediate formed by the addition of the triplet methylene to butene can probably undergo internal rotation before cyclization.

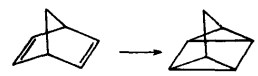
Hammond and coworkers have shown that, with the use of energy transfer at triplet levels, it is possible to induce sensitized photodecomposition of ethyl pyruvate into acetaldehyde and carbon monoxide with a much higher quantum yield than that obtained in the direct photolysis of this α-keto-ester[51]. They used benzophenone as an energy donor. The energy transfer is evidently very effective in this instance, since small additions of ethyl pyruvate (0.05 M) completely suppress the photoreduction of benzophenone to benzohydrol, which proceeds through the triplet state of benzophenone (see Section 6). β-Acetonaphthone, the triplet level of which (59 kcal mole^{-1} [52]) is considerably lower than the triplet level of ethyl pyruvate, does not sensitize the photodecomposition of this compound.

Berman and coworkers[53] have studied the ketone-sensitized photochemical decarbonylation of aldehydes, such as ethylenehexanal, heptanal, octanal, etc. Benzophenone, acetophenone, their chloro- and methoxy-derivatives, and 2-octanone, which have excitation triplet levels of about 70–75 kcal mole^{-1}, sensitize the photodecomposition, but acetophenone is ineffective, as with ethyl pyruvate. 2-Ethylenehexanal inhibits the photoreduction of benzophenone in propan-2-ol. The ratio of the rate constant for the transfer of energy from benzophenone to the aldehyde to the rate constant for the photoreduction is 70. It is interesting that for the inhibition by naphthalene of the photoreduction of benzophenone by alcohol this ratio is $\sim 3 \times 10^3$.[54]

3. SENSITIZED INTRAMOLECULAR REARRANGEMENTS

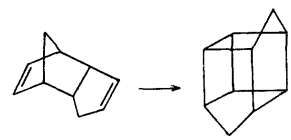
The first investigation of sensitized chemical reactions in solution was described in a paper published in 1931 by Weigert and Pruckner[55]. This dealt with the conversion of *o*-nitrobenzaldehyde into *o*-nitrobenzoic acid, photosensitized by acetone. When light of wavelength 313 nm acts on 0.05–2% solutions of *o*-nitrobenzaldehyde, the quantum yield for the rearrangement of aldehyde to acid ($\sim$ 0.5) is almost independent of concentration, although in a 2% solution the aldehyde absorbs three times as much light as acetone, but at 0.05% concentration, acetone accounts for 90% of all the light absorbed by the solution. Evidently all the energy absorbed by the acetone is transferred to the aldehyde.

In some instances sensitized reactions proceed with a higher quantum yield than the same reactions under the direct action of light. Thus, Hammond and coworkers[56] showed that the photochemical rearrangement of norbornadiene to quadricyclene:



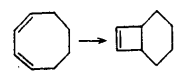
gives a much higher quantum yield when sensitized by such compounds as acetone, acetophenone, and benzophenone than the same reaction under the direct action of light[57].

Schenck and Steinmetz[58] showed that endodicyclopentadiene isomerizes to pentacyclo[5,2,1,$0^{2,6}$,$0^{3,9}$,$0^{4,8}$]-decane:



in the presence of acetone with a greater yield than that obtained under the direct action of light.

The photochemical isomerization of 1,3-cyclo-octadiene to Δ^7-bicyclo[4,2,0]octene[59]



can also be sensitized in the presence of benzophenone[60].

In all the intramolecular rearrangement reactions enumerated above ketones were used as sensitizers; as mentioned above, the probability of ketones passing into the triplet state when subjected to photoexcitation is very high. The rearrangements also appear to proceed through the triplet state. This may explain the higher quantum yields in the sensitized reactions, which, in contrast to the unsensitized reactions, appear to be a consequence of triplet-triplet energy transfer.

4. SENSITIZED *cis–trans* ISOMERIZATION

cis–trans isomerization relative to the ethylenic bond usually proceeds readily under the action of light[61]. Lewis and coworkers were the first to make a detailed study of photochemical isomerization; they studied the photoisomerization of stilbene in liquid and solid solutions[62]. Because of the stability of both its isomers, the substantial differences in their optical properties, and the high quantum yield in the *cis–trans* conversion, stilbene has also been frequently used in later investigations into the reaction mechanism of direct and sensitized isomerization. Lewis and coworkers compared data on absorption and fluorescence spectra and on quantum yields of the isomerization and concluded that when light is absorbed each isomer passes into its excited electronic level. Transition to the other isomeric form occurs by degradation of the electronic excitation to vibrational excitation, the energy of which is sufficient for rotation of groups in the molecule.

In subsequent papers[63–65], this picture was given concrete expression in accordance with Mulliken's ideas[66,67] on the excited state of ethylene and its derivatives. When the ethylene molecule is excited, the parallel position of the π-orbitals of the C=C bond ceases to be the position most favoured energetically and the orbitals are twisted through an angle of 90°. The triplet state then becomes

more stable than the singlet state. According to Dyck and McClure[63], because of conjugation of the ethylene bond with the phenyl rings in stilbene, a strictly perpendicular position of the π-orbitals in the excited state is not necessarily the most favourable position[63]. However, in the triplet state there must be much less restriction to rotation of groups about the ethylenic bond. A curious feature of the photoisomerization of *trans*-stilbene is the low activation energy of ~ 2 kcal mole^{-1}.[68,69] Stegemeyer suggests that a potential barrier separates the triplet states of *trans*- and *cis*-stilbene[68]. However, a number of other workers consider that this barrier exists in the transition of *trans*--stilbene from the first excited singlet state to the triplet state[63,69,70].

Investigation of the sensitized isomerization of stilbene has confirmed the view that *cis–trans* isomerization proceeds through the triplet state[71,72]. Hammond and coworkers[71] used acetophenone, benzophenone, and anthraquinone as additives in sensitizing the isomerization of stilbene in solution; the triplet levels of these compounds are higher than the triplet level of *cis*- and *trans*-stilbene[71]. In the sensitized reaction, the ratio of the concentration of the *cis*-isomer to that of the *trans*-isomer in a state of photo--equilibrium was found to be $[cis]_{equil}/[trans]_{equil} \simeq 1.5$. For direct isomerization under the action of light, $[cis]_{equil}/[trans]_{equil} \simeq 11$. The ratio of the absorption coefficient of the *trans*-isomer to that of the *cis*-isomer in the 313 nm region is 7.2. These workers consider that if the absorption coefficients were identical, triplet molecules of *cis*- and *trans*-stilbene would be formed at the same rate. In the photoequilibrium state, the ratio $[cis]_{equil}/[trans]_{equil}$ for the direct action of light would then be $11/7.2 \simeq 1.5$, that is, the same value as in sensitized isomerization. In the authors' opinion, this indicates that isomerization proceeds through the triplet state. Malkin and Fischer[69] determined the product of the rate constant for energy transfer from benzophenone to *trans*-stilbene and the lifetime of the benzophenone triplet molecules as $k_{AB}\tau = 2 \times 10^3$ litre mole^{-1}. Assuming that k_{AB} is determined by the diffusion rate (in methylcyclohexane $k_{AB} \simeq 3 \times 10^9$ litre mole^{-1} s^{-1}), they obtained $\tau = 5 \times 10^{-7}$ s. These workers also showed that *trans*-stilbene passes from the triplet state to the lower singlet level of the *trans*- or *cis*--form with about the same probability.

Hammond and coworkers obtained results of particular interest on the sensitized photoisomerization of stilbene, pent-2-ene, 1,2-dichloroethylene, 1,2-diphenylpropene, piperylene, and ethyl maleate–ethyl fumarate in the presence of energy-donor additives with triplet levels lower than the triplet levels of the acceptors[73–76]. The authors explain the occurrence of reaction in this instance by the possibility of "non-vertical" energy transfer to the triplet levels of the energy acceptors which correspond to the already "twisted" position of the groups in the molecule relative to the double bond. Here it is assumed that the triplet level of such a twisted molecule is lower than the triplet level to which the molecule passes when the position of the atoms is unchanged in accordance with the Franck–Condon principle (vertical transitions).

By plotting $[cis]_{equil}/[trans]_{equil}$ for the isomerizing acceptors against the energy of the triplet level of the sensitizers (E_T), Hammond and coworkers obtained peculiar "spectra"[76]. Fig. 3 shows an example of such a spectrum for stilbene. To interpret this spectrum, the authors put forward a scheme for the arrangement of the triplet levels of stilbene (Fig. 4). All the sensitizers with triplet

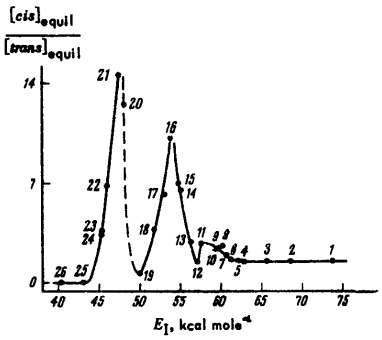


Fig. 3. Sensitized photoiosomerization of stilbene. Dependence of $[cis]_{equil}/[trans]_{equil}$ on the position of the triplet level of sensitizers:
1) acetophenone; 2) benzophenone; 3) thioxanthone; 4) anthraquinone; 5) flavone; 6) Michler's ketone; 7) 4-acetylbiphenyl; 8) 2-naphthyl phenyl ketone; 9) naphthalene-2-carbaldehyde; 10) 2-acetonaphthone; 11) 1-naphthyl phenyl ketone; 12) 1,4-naphthoquinone; 13) 1-naphthalene-1-carbaldehyde; 14) biacetyl; 15) penta-2,3-dione; 16) benzyl; 17) fluorenone; 18) duroquinone; 19) benzoquinone; 2) pyrene; 21) 1,2-benzanthracene; 22) benzanthrone; 23) acridine; 24) 3-acetylpyrene; 25) eosin; 26) 9,10-dibromoanthracene.

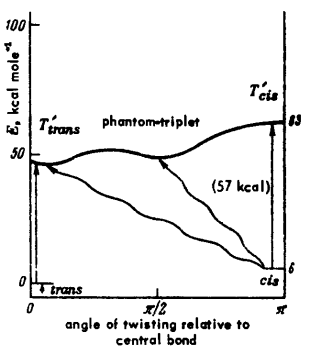


Fig. 4. Potential energy of rotation of stilbene in triplet state.

levels higher than the triplet levels of both stilbene isomers, that is, higher than 63 kcal mole^{-1}, probably give rise to vertical transitions to the triplet levels of both isomers. The ratio $[cis]_{equil}/[trans]_{equil}$ is then ~ 1.5. As the triplet levels of the sensitizers are reduced, the rate of energy transfer to *cis*-stilbene, the triplet level of which is higher than the corresponding level of *trans*-stilbene, apparently decreases faster than the rate of energy transfer to *trans*-stilbene. This leads to an increase in the ratio $[cis]_{equil}/[trans]_{equil}$.

However, at the 57 kcal mole^{-1} point (sensitizer: 1,4--naphthaquinone) corresponding to the O–O transition of *cis*-stilbene from the unexcited singlet state to the triplet state, a distinct minimum is observed (exact resonance). The second maximum (benzyl) corresponds to passage through the resonance condition for the vertical transition of *trans*-stilbene to the triplet level. The subsequent

minimum and maximum are due to non-vertical transitions to the corresponding triplet levels of twisted molecules. Finally, eosin and dibromoanthracene, in which E_T is less than 45 kcal mole^{-1}, can produce non-vertical transition and isomerization of *cis*-stilbene only, since the unexcited singlet level of the latter is 6 kcal mole^{-1} higher than in *trans*-stilbene. Similar spectra are also obtained for other acceptors that undergo isomerization.

Krongauz used the sensitized *trans–cis* isomerization of stilbene to study the triplet molecules of benzene in the liquid phase[77]. When dilute solutions of *trans*-stilbene in benzene are irradiated by light of wavelength 254 nm, which is absorbed almost entirely by the benzene alone, the stilbene is isomerized. In the concentration range studied (10^{-5} to 10^{-3} M), stilbene does not change the luminescence of benzene, that is, it does not deactivate the singlet excited benzene molecules. Energy transfer appears to take place between triplet levels. The lifetime of triplet benzene molecules ($\sim 10^{-6}$ s) and the lower limit of their quantum yield (0.1) were evaluated.

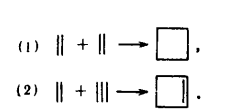
An important feature of this sensitization reaction is that the quantum yield for the isomerization of *trans*-stilbene is inversely proportional to the square root of the intensity of light absorption. This dependence is explained by the fact that the incident light is absorbed in a thin layer of solvent (half the light of wavelength 254 nm is absorbed by a benzene layer about 2.7×10^{-3} cm thick). The transfer of energy from benzene to stilbene also occurs in this layer, which leads to high stationary concentrations of triplet molecules in the thin layer and promotes the possible bimolecular deactivation of these molecules. By analogy with delayed fluorescence, it may be supposed that, when two triplet molecules of *trans*-stilbene interact, excited and unexcited singlet molecules are formed. On the basis of this explanation, the lifetime of *trans*-stilbene in the triplet state was found to be about 10^{-3} s.

Krongauz later used the sensitized isomerization of stilbene as a method of investigating triplet molecules in a liquid with the object of demonstrating the participation of triplet monomer molecules in the initiation of the photopolymerization of methyl methacrylate[78]. Bagdasar'yan suggested this mechanism for the photoinitiation of the polymerization of vinyl monomers[79]. When light of wavelength 254–265 nm acts on dilute solutions of *trans*-stilbene in methyl methacrylate, solvent-sensitized isomerization of the stilbene occurs. At the same time *trans*-stilbene inhibits the photopolymerization of methyl methacrylate, but has no effect on polymerization initiated by material initiators. Since the isomerization of stilbene is caused by energy transfer at triplet levels, it has been concluded that triplet monomer molecules participate in the initiation of photopolymerization.

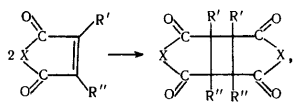
5. SENSITIZED DIMERIZATION AND POLYMERIZATION OF UNSATURATED COMPOUNDS

Bäckström and Sandros[9] studied the triplet-triplet transfer of energy from biacetyl to anthracene and found that, in addition to the quenching of the biacetyl fluorescene, a dimer of anthracene was formed.

Schenck and Steinmetz used sensitized dimerization for the synthesis of a large number of cyclobutane and cyclobutene derivatives[60,80,81]. The formation of cyclodimers by the interaction of two identical, or different, molecules containing C=C or C≡C bonds may be represented by the following scheme:



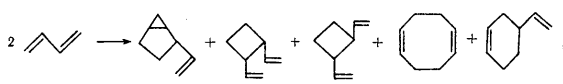
Various aldehydes, ketones, quinones, quinoid dyes, etc. have been used as sensitizers. The sensitization method has been used for the cyclodimerization of indene, coumarin, butadiene, etc., and also for reactions of the following type:



where R = H, CH_3; X = O, NH, N–C_6H_5, or N–C_6H_{11}. Many of these reactions do not occur under the direct action of light. Examples of sensitized reactions in which two different molecules interact include numerous reactions of the anhydrides of maleic and dimethylmaleic acids with benzene, thiophen, cyclohexene, chloro-derivatives of ethylene, furan, butyne, etc. Many of these reactions are recommended for preparative purposes.

After an examination of the mechanism of sensitization, Schenck and Steinmetz were inclined to favour the hypothesis that in many instances there is no transfer of energy but that intermediate biradical addition products are formed[60,82].

In dimerization reactions that occur under the direct action of light, a whole range of isomeric products is generally formed. On the other hand, sensitized reactions usually give a considerably lower number of isomers. For example, five different isomers are formed in the direct photodimerization of butadiene,



but in the sensitized reaction only the last three isomers are formed[56]. The ratios of the amounts of isomers formed depend on the nature of the sensitizer. In the cyclodimerization of isoprene, the distribution of dimerization products also depends on the nature of the sensitizer[83].

In the case of butadiene and isoprene, the ratio of the amounts of dimerization products is determined by the position of the triplet level of the sensitizer; the corresponding relationships form characteristic spectra with a minimum in the region $E_T \simeq 50$ kcal mole^{-1}.[108] The concept of sensitization of non-vertical transitions has been used in the interpretation of these spectra, and it has also been applied to sensitized *cis–trans* isomerizations. Hammond and coworkers[108] have put forward a number of objections to the view of Schenck and Steinmetz that sensitized dimerization proceeds through a stage in which intermediate biradical addition products are formed.

Norrish and coworkers have studied the sensitized photopolymerization of styrene[84,85]. The aromatic hydrocarbons anthracene, pyrene, and chrysene were used as sensitizers that absorb active light. It was shown by the flash photolysis method that additions of styrene (0.3–1.5 M) deactivate the triplet states of anthracene in solution. It was concluded that triplet molecules of anthracene

initiate the photopolymerization of styrene. The results of Norrish and coworkers do not lead unequivocally to this conclusion, since styrene can also effectively deactivate molecules in the singlet excited state[86].

The photoinitiation of polymerization of vinyl monomers by excited molecules of dye additives has been investigated[87-90]. Some workers consider that initiation is preceded by transfer of energy from the additive to the monomer[87]; others consider that polymerization is initiated by triplet molecules of the additive itself[85,88,90]. Solution of the problem is further complicated, because some additives enter into copolymerization or chain-transfer reactions with polymer radicals[78,85].

We are not, of course, here concerned with those reactions in which additive molecules are converted, as a result of decomposition or some other chemical reaction, into radicals that initiate polymerization. We shall only mention the example of sensitized decomposition of a radical initiator of polymerization which has been investigated by Überreiter and Sorge[87]. These workers carried out the photopolymerization of styrene in the simultaneoues presence of the two additives, Neutral Red and benzoyl peroxide, and they found that the dye (as an energy donor) sensitizes decomposition of the peroxide and thus accelerates photopolymerization.

6. OXIDATION–REDUCTION REACTIONS

The intermolecular transfer of energy has been used to elucidate the nature of excited states that participate in various photochemical oxidation–reduction reactions of organic compounds. The photochemical reactions of alcohols with quinones is an important example of these[91].

The photoreduction of benzophenone by alcohols, which was first carried out by Ciamician and Silber[92], proceeds with a high quantum yield and is used as a method for the preparation of benzopinacol. The process appears to occur according to the following scheme[93]:

$$(C_6H_5)_2CO + h\nu \longrightarrow (C_6H_5)_2CO^*,$$
$$(C_6H_5)_2CO^* + R_2CHOH \rightarrow (C_6H_5)_2\dot{C}OH + R\dot{C}OH,$$
$$R_2\dot{C}OH + (C_6H_5)_2CO \rightarrow R_2CO + (C_6H_5)_2\dot{C}OH,$$
$$2\,(C_6H_5)_2\dot{C}OH \rightarrow (C_6H_5)_2{-}\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}{-}\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}{-}(C_6H_5)_2.$$

States corresponding to $n \rightarrow \pi^*$ transitions appear to be the active excited states of carbonyl-containing compounds in these reactions[94].

Hammond and coworkers[12,95] found that the product of the rate constant for the interaction of excited benzophenone molecules with benzohydrol in benzene solution and the lifetime of the excited benzophenone molecules, $k_r\tau$, is about 20 litre mole^{-1}. Assuming that the maximal value of k_r is about 2×10^9 litre mole^{-1} s^{-1} (if the process is determined by the diffusion rate) these workers obtained a minimum value of 10^{-8} s for τ. In their opinion, the lifetime of the excited benzophenone molecules in the excited singlet state does not exceed 10^{-10} s, and they therefore concluded that triplet molecules take part in the reaction. The introduction of paramagnetic additives, such as oxygen and iron dipivaloylmethide, reduces the rate of reduction of benzophenone; this rate decrease is connected with the deactivation of the triplet state of benzophenone by these compounds. The more precise values of $k_r = 5 \times 10^6$ litre mole^{-1} s^{-1} and $\tau = 4 \times 10^{-6}$ s have been derived from kinetic results on the quenching of benzophenone triplet molecules by oxygen and the iron chelate.

Moore and Ketchum showed that naphthalene is about as effective in reducing the rate of reaction of benzophenone with benzohydrol as are the paramagnetic additives[96]. Naphthalene affects the photoreduction of benzophenone by propan-2-ol in the same way[54]. Since naphthalene is diamagnetic, and its first excited singlet level is higher than the corresponding level of benzophenone, the inhibiting effect of naphthalene is explained by the transfer of energy from benzophenone to naphthalene at triplet levels (see Section 1).

Later, Hammond and Leermakers showed that 2-acetophenone, piperylene, azulene, cyclo-octatetraene, biacetyl, and a number of other compounds that have triplet levels lower than the triplet level of benzophenone are about as effective as naphthalene in inhibiting the photoreduction of benzophenone[97]. These workers consider that this confirms the hypothesis that the rate of triplet-triplet energy transfer in these systems is controlled by diffusion, that is, energy is transferred in each collision of an excited benzophenone molecule with an acceptor molecule.

Using data on the kinetics of the benzophenone-sensitized phosphorescence of benzene solutions of biacetyl, Bäckström and Sandros[98] found that for benzophenone τ is about 2×10^{-6} s; it was assumed that the rate constant for triplet-triplet energy transfer, which is controlled by diffusion, is 1×10^{10} litre mole^{-1} s^{-1}. When propan-2-ol is used as a solvent, quenching of the phosphorescence occurs, evidently because of a reaction between the benzophenone and the alcohol; the lifetime of triplet benzophenone molecules is then reduced to 5.7×10^{-8} s.

The results obtained by Porter and coworkers by flash photolysis provide a direct proof that the triplet state participates in the reduction of benzophenone to benzpinacol[99,100]; it was shown by this method that the intermediates formed in the photolysis of benzophenone in benzene in the presence of propan-2-ol are ketyl radicals, $(Ph)_2{=}C{-}OH$. When naphthalene is added to the solution, the absorption band corresponding to the ketyl radicals disappears, and a new band characteristic of triplet naphthalene molecules appears[101]; virtually no benzpinacol is then formed. The lifetime of triplet benzophenone molecules in propan-2-ol, calculated from data on the kinetics of benzophenone consumption in the presence of naphthalene, is 6×10^{-8} s, which is in good agreement with the results of Bäckström and Sandros.

As in the reaction with benzophenone, the photochemical reaction between quinones and alcohols leads to the removal of hydrogen atoms from the alcohol and reduction of the quinone[102,103]. The following is a possible reaction scheme[104]:

$$Q + h\nu \rightarrow Q^*,$$
$$Q^* + R_2CHOH \rightarrow Q\dot{H} + R_2\dot{C}OH,$$
$$Q\dot{H} + R_2CHOH \rightarrow QH_2 + R_2\dot{C}OH,$$
$$2Q\dot{H} \rightarrow Q + QH_2,$$
$$2R_2\dot{C}OH \rightarrow R_2CO + R_2CHOH,$$

where Q is the quinone molecule and QH* is a semiquinone radical.

Obviously, the nature of the active excited state may differ in different quinones.

Bridge and Porter, who used the method of flash photolysis to study the intermediate particles formed in the photoexcitation of duroquinone in various solvents, showed that the disappearance of quinone triplet molecules and the formation of the semiquinone radical are independent processes that proceed at different rates [105]. From this it was concluded that the reduction of duroquinone proceeds through the excited singlet state. At the same time, the photoreduction of anthraquinone by propan-2-ol is greatly retarded in the presence of anthracene or naphthalene and it does not change in the presence of biphenyl [27]. The triplet levels of the first two hydrocarbons are lower, and that of the third is higher, than the corresponding anthraquinone level. For this reason, the inhibiting action of these additives is due to the transfer of energy from the anthraquinone triplet level, which appears to be the photochemically active level in this reaction.

In the presence of oxygen the mechanism of oxidation–reduction reactions may undergo substantial change [21]; oxygen itself then plays the part of the oxidant, and it is sensitized by the components that absorb light. In many instances (see, for example, Karyakin [106]), the reactions proceed through a stage in which intermediate peroxide compounds are formed. It is possible, however, that even here energy transfer from the sensitizer to oxygen is of considerable importance. Thus, Porter and Windsor [107] proposed the following scheme, which includes energy transfer, to explain the photo-oxidation of hydrocarbons by oxygen sensitized by anthracene:

$$A^T + O_2^T \rightarrow A^{S_0} + O_2^S,$$
$$O_2^S + RH \rightarrow R^{\cdot} + HO_2^{\cdot},$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot},$$

where O_2^T is the triplet ground state of oxygen and O_2^S is an excited singlet state.

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The material discussed in this review shows that the phenomenon of intermolecular transfer of excitation energy plays an important part in photochemical reactions of organic compounds in solution. In many instances the redistribution of the primarily absorbed light energy between the components of the solution considerably changes the course of the photochemical reaction. In particular, some reactions that proceed very slowly or not at all under the direct action of light can be induced by energy transfer from sensitized additives.

Sensitization and inhibition effects in photochemical reactions produced by intermolecular energy transfer are frequently used to elucidate the nature of excited states resulting from the action of light. An important advantage of sensitized photochemical reactions is their "cumulativeness", or their capacity to accumulate changes in the acceptor molecules that occur with the transfer of energy. This allows investigation of systems that are difficult to study by the luminescence method because of small quantum yields of the excited molecules under examination.

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OPTICALLY ACTIVE CHELATE COMPOUNDS

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I. INTRODUCTION

The exceptional sensitivity of optical rotation to various types of reaction (structural changes, intermolecular interaction, etc.) and the unique nature of the properties of optically active compounds is leading to the broad extension of

studies of this phenomenon in the most varied branches of chemistry, particularly in the chemistry of chelate† compounds. It is known, for example, that many complex processes which take place in living organisms with the participation of metals include the formation of optically active compounds.

Optically active chelate compounds, which can be studied by spectropolarimetry, have in recent years been the object of a large number of studies. For a long time the spectropolarimetric method did not find extensive application because of the lack of available reliable instruments. About 1955 this difficulty was overcome by the production of the Rudolph spectropolarimeter [2]. Analogous instruments have been produced comparatively recently in the USSR. [3,4]

The foundations of the spectropolarimetric method in Russia were laid by Chugaev in the early nineteen-hundreds, in the period of the completion of the theory of the structure of organic compounds. Chugaev set himself the task of establishing the relationship between the optical activity of a substance and its chemical structure [5]. At that time it was customary to relate optical activity to an asymmetric carbon atom.

Optical activity is not a property of an individual atom, but is a property of the asymmetric molecule as a whole. As a result of the unsymmetric arrangement of the ligands around the central metal atom, it was possible to separate optical isomers of chelate compounds of nickel $[Ni(bipy)_3]X_2 . yH_2O$, where bipy represents bipyridyl [6]; cobalt(III) with Schiff bases, 1,8-diamino-3,6-dithiaoctane, etc. [7-11]; ruthenium, $[Ru(bipy)_3]Cl_2 . 6H_2O$; [12] osmium, $[OsCl_2(bipy)_2]Cl_2 . 3H_2O$; [13] iron(III) with 8-(2-pyridylmethyleneamino)quinoline [14]; zinc with 8-quinoline-5-sulphonic acid [15]; chromium [16]; platinum [17,18]; and many others.

A large number of optically active chelate compounds, exhibiting rotatory power due to an optically active ligand, the asymmetry of the molecule as a whole, or the combined influence of both these factors, have now been prepared and studied. Since review papers on optically active chelate compounds cover chiefly material up to 1958, [19-22] our aim was to systematise the literature on the chemistry of optically active chelate compounds chiefly for the period 1959–1964 and also to outline the main tasks and problems which are being solved by the spectropolarimetric method.

II. PREPARATION OF CHELATE COMPOUNDS IN OPTICALLY ACTIVE FORMS

The preparation of chelates in optically active forms is the primary problem in the chemistry of chelate compounds. As noted above, chelate compounds may exhibit optical activity as a result of the presence in the molecule of a ligand which has been prepared beforehand in optically active form. In a number of instances, however, the ligand may not contain an asymmetric centre, and the molecule as a whole becomes asymmetric after the formation of the chelate. It thus becomes necessary to separate the optical isomers of the previously-prepared chelate compound. This problem is extremely complex and its solution is directly related to the specific nature and properties of the chelate compounds.

Two main methods are used for the resolution of chelate compounds. The first method is based on the chemical reaction of optically-resolving agents with the chelate molecules, which should either be ionic or contain some functional group. In this the resolution involves the formation of diastereoisomers, which are then separated by fractional crystallisation, extraction, or chromatography. The most widely used optically active resolving agents are tartaric acid [23,24], (+)-nitrocamphor [16], antimony oxide (+)-tartrate [13,14,25], arsenic oxide (+)-tartrate [26], etc.

The resolution of some ionic chelate compounds — for example, tris-1,10-phenanthrolineruthenium(II) perchlorate — was achieved owing to the difference in the solubility of their antipodes in the presence of optically active additions (*d*-bromocamphorsulphonate) [27,28]. Recently optically active chelate compounds have been successfully used for resolving ionic chelates [29-32].

The second method of resolution, applied chiefly to "neutral" compounds, that is, compounds which are not ionic and contain no functional groups, is based on the selective adsorption of the chelates on quartz, starch, lactose, and other adsorbents. The resolution of (±)-Cr(HFA), where HFA is the fluoro-derivative of acetylacetone, has been carried out successfully by gas chromatography on quartz [33].

Chelate compounds of copper and nickel with β-keto--imines have been resolved by chromatography on D-lactose [34]. The same adsorbent gave satisfactory results in the resolution of oxobis-[4,4'-(propylenedi-imino)di-(2--pentanone)vanadium(IV). [35] Alumina treated with (+)-tartaric acid can be used as well as quartz for the resolution of Cr^{3+} and Co^{3+} acetylacetonates [36]. An interesting paper by Ferroni and Cini [37] describes the use of crystals of sodium *d*- and *l*-chlorate for the resolution of bis(benzoylacetonato)beryllium(II).

Recently, selective adsorption has also been used for the resolution of ionic chelates. Thus Dwyer and coworkers [38,39], in a study of compounds of the type $[Co(\pm)pn_2en]Cl_3$, $[Co(\pm)pnen_2]Cl_3$, $[Co(\pm)pn]Cl_3$, etc., where en represents ethylenediamine and pn propylenediamine, resolved the products on a cellulose column.

Other methods and reagents which are proving effective for the resolution of chelates are equally interesting. Harada and Fox [40] resolved the copper complex of aspartic acid by the introduction of a seed crystal of the optically active chelate. Interesting data have also been published [41] on the resolution of chelates by diffusion in liquids with asymmetric molecules.

Attempts to find new reagents and methods for the resolution of chelate compounds, particularly the search for new adsorbents, naturally deserve constant attention.

III. THE USE OF SPECTROPOLARIMETRY AND POLARIMETRY FOR THE STUDY OF CHELATE COMPOUNDS

1. Study of Redox Reactions, Racemisation, and Substitution in Chelates

Measurements of the rate of change of the optical rotation were used by Dwyer and Gyarfas [42] in a study of the dynamic equilibrium between the oxidised and reduced forms of the ions $Os(bipy)_3^{2+}$ and $Os(bipy)_3^{3+}$. This work was continued and refined by Eichler and Wahl [43], who studied

† We use the term "chelate" to describe metallocyclic compounds, in which the metal–ligand bonds may be different in character. A more detailed discussion of nomenclature has been published [1].

the rate of electron exchange in $Fe(phen)_3^{2+}-Fe(phen)_3^{3+}$, where phen = phenanthroline, and $Os(bipy)_3^{2+}-Os(bipy)_3^{3+}$ systems from the change in optical rotation and by using isotopic tracers.

Dwyer and Sargeson[44] described the measurement of the rate of electron transfer from the change in the dispersion of the rotation of the $Coen_3^{2+}-Coen_3^{3+}$ system. A detailed study of rates of electron transfer was made by Im and Busch[45,46], who divided the systems studied into two categories. The first consists of systems in which the absolute configuration is not preserved on electron transfer. As an example, the dependence of the racemisation of ethylenediaminetetra-acetatocobaltate(III) on temperature, pH, and concentration was studied. The hexadentate complex d-$[Co^{III}EDTA]^-$, where EDTA represents ethylenediaminetetra-acetate, undergoes racemisation at 100°, 90°, 85°, and 74° and the racemisation is catalysed by $[Co^{II}EDTA]^{2-}$ ions. We thus have two processes

$$d\text{-}[Co^{III}EDTA]^- \rightleftharpoons l\text{-}[Co^{III}EDTA]^-,$$

$$d\text{-}[Co^{III}EDTA]^- + [Co^{II}EDTA]^{2-} \rightleftharpoons [Co^{II}EDTA]^{2-} + l\text{-}[Co^{III}EDTA]^-.$$

The second category consists of systems in which the absolute configuration is preserved on racemisation, for example, 1,2-propylenediaminetetra-acetatocobaltate(III).

Racemisation of the ionic complex $[Coen_3]^{3+}$ in the presence of active carbon takes place as a result of a redox reaction[47]. By making use of electron exchange and the difference in the solubilities of the diastereoisomers of the tris(ethylenediamine)cobalt(III) ion, Busch[48] increased considerably the yield in the resolution of this ion.

The spectropolarimetric method has also been used successfully to measure the rate of exchange of the free ligand 1,2-propylenediaminetetra-acetic acid (PDTA) with its complex[49]:

$$[M(+)PDTA]^{4-} + l\text{-}PDTA \rightleftarrows [M\,l\text{-}PDTA]^{4-} + d\text{-}PDTA,$$

where M = Cu, Ni, Co, etc. It is obvious that the rotation falls to zero when half of the ligand has reacted.

The problem of racemisation is related to the problem of electron exchange and ligand exchange in chelate compounds. Redox reactions are one factor responsible for the racemisation of chelate compounds. This phenomenon has been examined in detail by Lewis and Wilkins[22] and in a number of recent papers. It has been established that the racemisation of certain compounds, for example, *cis*-chloroaquobis(ethylenediamine)cobalt(III)[50,51] and *cis*-bis(oxalato)diaquochromate(III),[52] takes place as a result of the isomerisation of the optically active *cis*-compound into the symmetrical *trans*-compound. In other examples the racemisation is brought about by dissociation of the chelate. For example, the tris(acetylacetonato)silicon cation undergoes racemisation as a result of degradation by hydrolysis[53]. Dissociation is responsible for the racemisation of a large number of nickel chelates with phenanthroline and bipyridyl[28,44-56]. Brown and Ingold[57] used polarimetry to study the kinetics of the replacement of chloride ions in the *cis*-dichlorobis(ethylenediamine)cobalt(III) ion.

An important problem concerns the behaviour of chelate compounds in various chemical reactions, particularly substitution. In a number of instances spectropolarimetry makes it possible to establish whether the reaction involves the chelates themselves or free ligands liberated as a result of dissociation of the chelate. Study of the bromination and diazo-coupling of optically active catechol-arsenic(IV) chelates[58] showed no significant change in optical activity and configuration, from which it was concluded that the reaction involves the chelates themselves.

Preservation of the optical activity is also observed in electrophilic substitution (chlorination, bromination, nitration, etc.) in optically active tris(acetylacetonato)-compounds of Cr^{III}, Co^{III}, and Rh^{III}.[59] Thus the chelate compound reacts as a single aromatic system, since otherwise, racemic products would have been obtained after the reactions.

2. Quantitative Polarimetric Determination of Metals and Ligands in Chelates

The use of polarimetry for the quantitative determination of optically active natural products is well known. This method can also be used, however, for the quantitative determination of optically inactive compounds. In 1957, Freegarde[60] determined the metal ions Ag^+ and Fe^{3+} by means of the optically active reagent (+)-tartaric acid. Freegarde measured the rotation of a (+)-tartaric acid solution before and after the addition of a weighed specimen of the substance, which formed a precipitate with the optically active reagent.

Complex formation by molybdic acid with maleic and tartaric acids, mannitol, sorbitol, and other compounds has been used for the polarimetric determination of the latter in the presence of various other optically active compounds[61].

Haas and Faber[62] used (+)-tartaric acid for the quantitative determination of molybdenum by a polarimetric method. The ability of the Cu^{2+} ion to form a complex with L-(+)-histidine has been used for the spectropolarimetric determination of the metal ion and the optically active ligand[63].

3. Study of Chelate Formation and the Nature of the Bonding in Chelates

The study of optical activity assists in the deeper penetration into the essential features of the processes taking place on chelate formation and in the investigation of very slight molecular changes which cannot be observed by other methods.

By studying the optical rotatory power of L-propylenediamine in the presence of different quantities of metal ions (Zn^{2+}, Cd^{2+}, Hg^{2+}, or Ag^+) it is possible to gain information on chelate formation from the change in rotation. The optical activity of L-propylenediamine remains unchanged in the presence of Ba^{2+} and Mg^{2+} ions, apparently due to the absence of chelate formation[64].

Larsson[65] used polarimetry to study various outer-sphere complexes of (+)-tris(ethylenediamine)cobalt(III). It is a familiar fact that change in the composition of the second coordination sphere of complexes of transition metals (sulphate, chloride, etc. ions) does not produce marked changes in the absorption spectra, whereas the optical rotation of the ionic complexes depends to a marked extent on the nature of the counter-ion. Larsson measured the optical rotation of (+)-$[Coen_3]^{3+}$ in aqueous solutions with gradual increase in the concentration of sulphate,

thiosulphate, fluoride, chloride, and perchlorate ions, and observed a rotation minimum in the first two instances, indicating the formation of outer-sphere complexes.

A change in the dispersion of the rotation was also observed when optically inactive ions were added to (-)-*cis*-oxalatobis(ethylenediamine)cobalt(III) and (-)-tris(ethylenediamine)chromium(III) ions[66]. A polarimetric study of the conditions of the reaction of orthotellurate with (+)-tartrate established that a compound with 1:1 composition is obtained[67]. Polarimetric study of the Th^{4+}–tartaric acid system led to the conclusion that a stable chelate compound with the 1:1 composition is formed[68]. In analogous fashion, Chinese authors[69] established the existence of a cobalt tartrate with 1:1 composition by observing the change in the rotatory power, absorption coefficient, and refraction of the system.

The study of optical activity helps to solve the problem of the nature of the bonding in chelate compounds[70]. For example, the lack of success in attempts to resolve tris-(oxalato)manganates and tris(oxalato)ferrates[71] may be attributed to ionic bonding between the metal and the coordinated groups in these chelate compounds. In compounds which can be obtained in optically active form, these bonds are covalent.

4. Study of the Phenomenon of Stereospecificity in the Chemistry of Chelates

The phenomenon of stereospecificity has been observed in the study of optically active chelate compounds. This problem has been examined in a number of monographs[20-22] and reviews[72-76].

The problem of stereospecificity is related to the chemistry of mixed chelate compounds, in which different ligands are coordinated around the central metal atom. Mixed chelate formation is fairly common among ionic chelates and there is no need to deal specially with this question[77-80]. It may be noted that mixed tris-bidentate chelate compounds can be prepared by three methods: by adding ligands to the bis- or mono-chelate, by replacing ligands in tris-chelates, or by direct preparation. These compounds have been the subject of many studies[26,81].

The preparation of mixed chelates presents no obstacles so long as optically inactive ligands are dealt with. The preparation of chelates containing optically active ligands introduces the effect of stereospecificity, as a result of which some possible isomers (*Dlld*, *Ldll*, etc.) of these compounds are obtained in very small yield or not at all. Thus in the reaction of racemic propylenediamine (pn) with platinum(IV) chloride, Smirnoff[82] was able to obtain only two compounds *D*-$[Pt(L\text{-}pn)_3]^{4+}$ and *L*-$[Pt(D\text{-}pn)_3]^{4+}$.

Bailar and his coworkers[83] found that mixed isomers are probably formed, but undergo disproportionation with the formation of the products which were isolated by Smirnoff. The similar formation of a limited number of isomers of tris-(*trans*-1,2-diaminocyclopentane)cobalt(III) by Jaeger and Blumendal[84], who consider that two or more of the ligands in the chelate compound usually have the same configuration, that the chelate exists in a single configuration, and its sign of rotation may be the same as or opposite to that of the ligand.

Subsequent studies refuted this opinion to some extent. Lifschitz[85], for example, prepared tris-(D-alanine)-cobalt(III), from which two α-forms *Dddd* and *Lddd* and one β-form were isolated. The fact that the two α-forms have equal stabilities suggests that the stereospecific effect is not very strong in amino-acid chelates. Bailar and coworkers[86,87] found that the carbonatobis-(L-propylenediamine)cobalt(III) ion exists in both *D*- and *L*-forms, and that the configuration of its salt depends on the method of crystallisation. Another paper[88] reports the existence of both the (+)-tartratobis-(L-propylenediamine)cobalt(III) and (-)-tartratobis-(L-propylenediamine)cobalt(III) ions, but the stabilities of these isomers are different.

Extensive studies of the phenomenon of stereospecificity have been made by Dwyer and coworkers. Ionic chelates of Co^{III} with D- and L-propylenediamine (*Dlll* and *Lddd*) have been prepared and the equilibria between the isomers *Dddd* ⇌ *Lddd* and *Dlll* ⇌ *Llll* have been studied[89]. Analogous isomers of Pt^{IV} were prepared[90]. An attempt to prepare chelates with mixed ligands by the reaction of dichlorobis(ethylenediamine)cobalt(III) chloride with L-propylenediamine was unsuccessful and gave a mixture of the chlorides $[Coen_3]Cl_3$ and $[Co(L\text{-}pn)_3]Cl_3$.[91] The reaction of tetrachloro(L-propylenediamine)platinum(IV) and tetrachloro(ethylenediamine)platinum(IV) with ethylenediamine and D-propylenediamine, however, led to the preparation and resolution of the mixed chelates $[Pten_2(L\text{-}pn)]Cl_4$, $[Pt(L\text{-}pn)_2en]Cl_4$, and $[Pt(D\text{-}pn)_2(L\text{-}pn)]Cl_4$. It was pointed out that unsuccessful attempts to isolate mixed chelates are apparently due not to differences in the stabilities of the chelates but to the establishment of an equilibrium between all possible isomers in the course of the reaction. This led to the isolation of the thermodynamically more stable isomers $[Pt(L\text{-}pn)_3]Cl_4$ and $[Pt(D\text{-}pn)_3]Cl_4$, which predominate in the mixture, whereas the small quantities of the mixed isomers could not be detected. It was suggested that the equilibrium is established either as a result of the formation of intermediate 7- or 8-covalent chelates, or as a result of the catalytic influence of small quantities of Co^{II} and Pt^{II} chelates. Recently, Dwyer and coworkers[93] described the preparation of a mixture of isomers, from which the following were separated by chromatography on a cellulose column: *L*-$[Co(-)pn_3]Cl_3$, *L*-$[Co(-)pn_2en]Cl_3$, *L*-$[Co(-)pnen_2]Cl_3$, *D*-$[Co(-)pn_3]Cl_3$, *D*-$[Co(-)pn_2en][ClO_4)_3$, and *D*-$[Co(-)pnen_2](ClO_4)_3$. It is considered that the degree of stereospecificity of the chelates is a property chiefly of the ligands and may vary from almost zero, for sodium bis(oxalato)-L-propylenediaminecobaltate(III)[94] to the almost complete stereospecificity of the chelates with propylenediaminetetra-acetic acid[95].

Partial stereospecificity was observed in a study of cobalt(III) chelates with 4-methyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane[25]. It was established that the dextrorotatory isomer of the ligand gives chiefly the laevorotatory form of the chelate (85%), whereas the laevorotatory isomer gives the dextrorotatory form of the chelate. In a continuation of their study of stereospecificity, Dwyer and coworkers[38] recently described the isolation of various mixed chelates of Co^{III} with propylenediamine and gave the equilibrium constants for the systems

$$D\text{-}[Co(+)pn_3]^{3+} \cdot L(Co(-)pn_3]^{3+}/D[Co(+)pn_2(-)pn]^{3+} \times L[Co(-)pn_2(+)pn]^{3+}=1.0$$
$$D\text{-}[Co(+)pn_2(-)pn]^{3+}/L[Co(+)pn_2(-)pn]^{3+}=2.4$$
$$D\text{-}[Co(+)pn(-)pn_2]^{3+} \cdot L=[Co(-)pn(+)pn_2]^{3+}/D[Co(-)pn_3]^{3+} \cdot L=[Co(+)pn_3]^{3+}=6.1.$$

The stability of the isomers and their relative concentration in the mixture were explained on the basis of the possible conformations of the propylenediamine ring.

As well as being of purely theoretical importance, the phenomenon of stereospecificity has found practical appli-

cation. Bailar and coworkers[83] suggested that if the reaction between an optically active chelate and an excess of a racemic coordinating substance is selective, that is, if the chelate can accept only one optically active isomer from the racemate, resolution of the racemic ligand should be observed. The first experiments did not give satisfactory results, however. Later[88], partial resolution of racemic tartaric acid was achieved by heating the cobalt chelate $[Co(L\text{-}pn)_2(rac\text{-}tart)]Cl$ in aqueous solution with an excess of L-propylenediamine. The latter replaces the (-)-tartrate ion in the chelate, whereas the (+)-tartrate ion is much more firmly held in the coordination sphere, proving that the configurations of (+)-tartaric acid and L-propylenediamine are identical. Partial resolution of racemic mixtures of organic acids (tartaric, α-chloropropionic, and lactic) was achieved using the carbonatobis(L-propylenediamine)cobalt(III) ion[96]. In all instances the dextrorotatory form of the acid enters the coordination sphere more readily than the laevorotatory form, and this leads to resolution. This reaction can also be used to determine the configuration of optically active acids. An attempt to resolve racemic tartaric acid by the reaction of its silver salt with *trans*-dichlorobis[(-)-stilbenediamine]-cobalt(III) nitrate was unsuccessful[97], however.

Sarma and Bailar[98] described the partial resolution of diamines, amino-acids, and dibasic acids by coordination with an optically active chelate. Stereospecificity has also been used successfully to prepare optically active chelate compounds[29,99,100]. For example, when (±)-$[Co(EDTA)]^-$ is treated with L-propylenediamine, the amine reacts with (-)-$[Co(EDTA)]^-$, leading to partial resolution of the chelate. Stereospecific reactions were recently used to prepare optically active forms of propylenediamine[101] and propylenediaminetetra-acetic acid[102].

The phenomenon of stereospecificity in non-ionic optically active chelate compounds of the bis-[*o*-(α-phenylethyliminomethyl)phenolato]copper type was studied by Terent'ev and coworkers[103]. In a study of the possibility of preparing chelates with irregularly paired ligands, in which the metal atom would be combined with two different molecules of a Schiff base ligand, it was established that for the systems studied the compounds with regularly paired ligands are favoured energetically.

A mixture of (-)-*o*-(α-phenylethyliminomethyl)phenol and (+)-*o*-(α-phenylethyliminomethyl)phenol in the presence of an excess of one of the forms was taken for the original ligands, and the chelate formation was carried out with copper and nickel; it was concluded that the products are always the compounds in which the metal is coordinated to ligands with one configuration, to give chelates with regularly paired ligands (*ll* or *dd*). An interesting feature is that these compounds can be formed by crystallisation of the double crystal-racemates *ll*×*dd*. This intramolecular racemisation leads to separation of a racemic fraction of the ligand in the form of the chelate, and the remaining uncombined fraction of the ligand is enriched in one of the optically active forms (*l* or *d*) taken in excess. This makes it possible to carry out the further purification of incompletely resolved amines and to obtain them in optically pure form.

5. The Configuration of Chelate Compounds

The study of optical rotatory power assists in the solution of the problem of the three-dimensional structure of a number of chelate compounds. In some instances the production of optical activity can be explained if it is assumed, following Werner[104], that the chelate compounds of elements with a coordination number of 6 have an octahedral structure whereas compounds with coordination number 4 have a tetrahedral or square-planar structure. Thus to explain the optical activity of *meso*-stilbenediamineisobutylenediamineplatinum chloride, Mills and Quibell[105] suggested that the bonds have a planar arrangement, since only then is the molecule asymmetric. With tetrahedral arrangement of the bonds, a plane of symmetry appears, so that the optical activity disappears.

The tetrahedral configuration of some beryllium chelates was confirmed by the successful resolution of their optically active isomers. Burgess and Lowry[106] observed the existence of optical isomers for benzoylcamphor complexes of beryllium, whose solutions exhibit mutarotation. This phenomenon was attributed to the gradual disappearance of the optical activity associated with the beryllium atom, which is the centre of the asymmetry.

Mills and Cotts[107] studied chelate compounds of beryllium, copper, and zinc with benzoylpyruvic acid; the optical isomers were separated using strychnine and brucine. They obtained an optically active solution almost free from alkaloid, but this rapidly underwent racemisation. Bis-(benzoylacetonato)beryllium, resolved by Busch and Bailar[108] by shaking a benzene solution of the chelate with optically active quartz powder, was found to be more stable.

The partial resolution of the tris(oxalato)germanate(IV) ion[109] proves the octahedral arrangement of the bonds in this ion and their covalent character. The successful resolution of bis(*o*-diethylphosphinophenyldiethylarsine)-copper(I) indicates that this compound has tetrahedral configuration[110]. The tris(biguanidine)-chelates of Co^{III} and Cr^{III}, like the tris(ethylenediamine)-chelates, have an octahedral configuration in which there are no elements of symmetry, and this was confirmed by separation of their optical isomers[23]. Ramaiah and coworkers[35] suggested that the five-coordinate chelate oxobis-[4,4′-(propylene-di-imino)di-(2-pentanone)]vanadium(IV) has a plane-pyramidal structure. In this instance the compound should exist in the form of optical isomers, and this was in fact proved. The partial resolution of the optical isomers of the β-keto-imine chelates of copper and nickel by a chromatographic method confirms that these compounds have tetrahedral configuration[34]. These and other examples[111,112] confirm that the existence of optical isomers provides a means of investigating the configuration of chelate compounds.

An important problem which has recently attracted the attention of research workers[113] is the determination of the absolute configuration of optically active chelates. A very important step in this direction was taken by Japanese scientists[114], who used X-ray diffraction methods to determine the absolute configuration of the *D*-(+)-$Coen_3^{3+}$ ion.

Later, Ballard and coworkers[115] proposed a new criterion for establishing absolute configuration, based on the sign of the optical rotatory power of the chelate in the long-wave range of the spectrum and on the sign of the rotatory power of the ligand[116]. Saito and coworkers gave data on the determination of the absolute configuration of the $[CoCl_2(L\text{-}pn)_2]^+$ [117] and *L*-$[Co(L\text{-}pn)_3]^{3+}$ [118] ions. The determination of the absolute configuration of some chelates is important since it makes possible the rapid determination of the configuration of many other analogous

compounds by comparison of their absorption spectra and rotatory dispersion curves. Japanese authors [119-122] have pointed out that if two optically active chelate compounds have similar bond character and hence similar stabilities, the sign of the Cotton effect should depend only on the absolute configuration. Compounds with the same absolute configuration should give Cotton effects with the same sign. This comparison of the rotatory dispersion curves of chelate compounds with known and unknown configurations has been used [24,36,76,123,124] to determine the configuration of chelates.

Optically active quartz and various other solids are being used successfully for the resolution of chelate compounds [37]. Bailar [125] has pointed out that if it were possible to show that a relationship exists between the configuration of quartz and the configuration of the isomer which is adsorbed by it, this would provide a simple method for determining the configuration of optically active substances.

The configuration of non-ionic optically active chelate compounds was discussed by Pfeiffer [126]. In a study of the rotatory dispersion curves for a number of chelates based on salicylaldehyde and various optically active amines and diamines and containing optically active formylcamphor, Pfeiffer reached the following conclusions.

1. The Cotton effect is shown by optically active chelate compounds of this type in the visible range of the spectrum only when a chromophoric metal atom is present.

2. As far as the manifestation of the Cotton effect is concerned, dicyclic and tricyclic compounds are in principle equivalent.

3. The position of the asymmetric carbon atom relative to the metal atom in the compounds studied plays no significant part in the manifestation of the Cotton effect.

Since the rotatory dispersion curve shows an anomalous shape when a metal is added to a Schiff base, it was concluded that in addition to the asymmetric carbon atom there should be another centre of asymmetry — the metal atom — and that it is the latter which produces the Cotton effect. From this Pfeiffer concluded that the chelates considered have tetrahedral configuration. Chelate compounds of the same type but containing no asymmetric carbon atom have planar configuration. Pfeiffer considered that the vicinal effect cannot be responsible for the Cotton effect. In an analysis of this work by Pfeiffer, Martell and Calvin [20] consider the rejection of the vicinal effect to be premature. The vicinal effect is apparently responsible for the anomalous shape of the rotatory dispersion curves. Evidence against tetrahedral configuration for these compounds is also provided by the fact that they could not be separated into optical isomers with respect to the central metal atom.

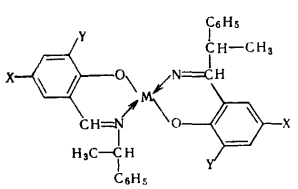
Thus Pfeiffer, on the basis of the normal rotatory dispersion curve for the nickel–formylcamphor complex, concluded that this chelate has square-planar configuration [126]. Later, however, French and Corbett [127] recorded the ultraviolet spectrum and rotatory dispersion curve and found that the rotatory dispersion curve shows a maximum at $\lambda = 3162$ Å, due to the absorption band of the nickel centre in the molecule. Measurement of the magnetic susceptibility of this compound in the solid state and in methanol solution shows that it is paramagnetic. On the basis of the data obtained, it was concluded that the nickel–formylcamphor complex has tetrahedral configuration. Subsequent study [128] of the absorption spectra, rotatory dispersion, and magnetic susceptibility of bis(formylcamphor)ethylenediaminenickel led to the conclusion that this compound has planar configuration in the solid state, but that in methanol solution, under the influence of the asymmetric centre present, equilibrium is established between the two configurations: planar and tetrahedral.

From these data it can be seen that the mere presence or absence of the Cotton effect does not provide proof for tetrahedral or planar configurations respectively in chelate compounds. In these compounds the central metal atom is a chromophore which reacts with the asymmetric centre in the molecule. The absorption band corresponding to the metal atom is optically active and a Cotton effect appears in this range of the spectrum.

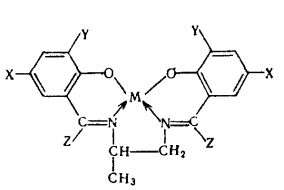
Lifschitz [129] in a study of the rotatory dispersion of chelate compounds, examined the question of the relationships which should exist between the chromophore and an optically active centre for production of the Cotton effect. He considers that in compounds containing optically active coordinated groups, a Cotton effect in the range of the absorption band of the central metal atom is observed only when the asymmetric atom is a member of a ring formed through the central atom by means of "inner-complex bonding (that is, where the metal atom is attached to the organic molecule by means of a principal valency and a subsidiary valency)". Lifschitz emphasises the difference in the behaviour of the copper and nickel chelates. Thus the compounds of $[Cu(L\text{-}pn)_2]^{2+}$ give an anomalous rotatory dispersion curve, whereas the compounds of $[Ni(L\text{-}pn)_2]^{2+}$ give a normal curve. Lifschitz considers that for the nickel chelate it is necessary to assume a symmetrical structure in which the rotation is due entirely to the optically active propylenediamine molecules present. The unique behaviour of copper is attributed to the possibility of partial asymmetric synthesis.

A review by Mat'ë [130] gives several examples from the literature which have been attributed to partial asymmetric synthesis, and points out that in every instance where a complex capable of existing in two enantiomorphic forms is obtained, it is necessary to investigate carefully whether the Cotton effect arises from a bond between an active molecule and the central atom or is due to partial asymmetric synthesis.

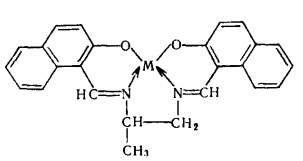
Recent papers by Terent'ev and coworkers [131-133] give the results of spectropolarimetric studies of chelates with structures A, B, C, D, and E, with optically active *o*-hydroxyaldimines and *o*-hydroxyketimines.



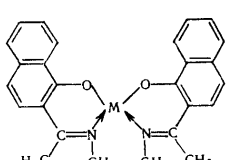
(A) X = H, Cl, Br, NO_2; Y = OCH_3, H; M = Cu, Ni, Co



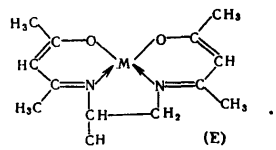
(B) X = H, Cl, Br, NO_2; Y = OCH_3, H; Z = CH_3, H; M = Cu, Ni, Co



(C)



(D)



(E)

On the basis of a comparison of the rotatory dispersion curves for these compounds, it was concluded that non-vicinal (distant) substituents (X, Y) in the chelates have little influence on the rotatory dispersion. The introduction of a vicinal substituent ($Z = CH_3$) in the metal-containing ring on going from the hydroxyaldimine derivatives to the hydroxyketimine derivatives, however, leads to a sharp increase in the absolute values of the molecular rotation without altering significantly the nature of the rotation, due to the difference in the degree of coplanarity of the chelate compounds.

Although spectrophotometry has been unable to record these fine changes in molecular structure, the conclusions reached on the basis of spectropolarimetric studies have been confirmed by data from the EPR spectra[134].

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It can be seen from the foregoing that the use of polarimetry and spectropolarimetry in the study of optically active chelate compounds opens up promising possibilities. The high sensitivity of these methods makes it possible in a number of instances to record fine changes in a molecule, difficult to detect by other methods.

The possibilities of the spectropolarimetric method in the chemistry of optically active chelate compounds are far from being exhausted, however. The increase observed every year in the number of studies in this field and the isolation of new chelates in optically active form enable us to hope that new properties and phenomena making it possible to reach a deeper understanding of the chemistry of optically active chelate compounds will be discovered and studied.

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MASS SPECTRA AND MOLECULAR STRUCTURE OF HYDROCARBONS

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I. INTRODUCTION

Modern ideas on the molecular structure of organic compounds are to a large extent linked with the study of physical properties, such as absorption spectra in all regions from the ultraviolet to the microwave, dipole moments, atomic and electronic polarisation, etc. In the last two decades a new method for investigating organic compounds — molecular mass spectrometry — has been developed; this deals with the interaction of molecules and electrons. The overall relative probability of the formation of various ions that arise when a molecule is bombarded with slow (20–70 eV) electrons is characteristic of the stability of the molecule, and, what is very important for the organic chemist, of its structure, since the possible rupture of a given bond depends mainly on the distribution of electron density.

The formation of mass spectra is generally considered from the point of view of the Franck–Condon principle[1], according to which the first act in any inelastic collision between an electron and a molecule is electronic excitation of the latter, which occurs as an electronic transition while the distance between nuclei remains unchanged. In the inelastic collision of an ionising electron with a molecule, one of the valence electrons is removed and a molecular ion corresponding to the molecular weight and empirical formula of the compound is formed. Electrons acting on the molecule in the ion source of the mass spectrometer usually possess energy of several tens of electron volts; therefore, in the bombardment of polyatomic molecules, in addition to ionisation, decomposition of molecular ions occurs with rupture of C–C and C–H bonds and the formation of ionic fragments, which may also decompose in turn. This multiplicity of processes is responsible for the complexity of the mass spectra of polyatomic molecules with their multiplicity of lines.

The stability of organic molecules to electron impact is characterised by the probability of decomposition of molecular ions[2], W_Z, and is determined by the ratio of the number of molecular ions (I_{mol}) to the number of fragmentation ions (ΣI_{frag}): $W_Z = \Sigma I_{frag}/(I_{mol} + \Sigma I_{frag})$. The value of $W_M = (1 - W_Z)$ determines the stability of the molecule to electron impact.

This ratio, in turn, reflects the rate of decomposition of the molecular ion; since the time between the formation of ions and their detection is usually 10^{-5} s, the absence of particular molecular-ion peaks in the mass spectrum indicates that these ions have a short life. The rate of decomposition of the molecular ion is a function of the energy acquired by the ion during its formation; when the energy of the ionising electrons falls to a value close to the ionisation potential of the molecule, the proportion of molecular ions is increased in relation to that of fragmentation ions.

The ionisability of molecules and radicals formed in the rupture of chemical bonds is characterised by what is termed complete ionisation, which represents the quantity of ions formed by unit quantity of the compound[3]. It is determined by the sum of the intensities of all the peaks in the spectrum multiplied by the coefficient of sensitivity of the strongest peak; the latter is expressed in units of ion current referred to unit pressure.

In addition to the ions formed by simple rupture of bonds, the mass spectra of nearly all molecules containing more than two carbon atoms show the presence of ions that are produced as a result of rearrangement of atoms at the moment of dissociation. Rearrangements with migration of a hydrogen atom are observed very frequently[4]. The activation energy of rearrangements in ions is low and commensurable with the activation energy of rearrangements in neutral molecules; accordingly, rearrangements in the molecular ion proceed comparatively easily[3]. With hydrocarbons the difference in activation energies of various rearrangements is very small, and therefore competing reactions lead to the formation of diverse fragments.

Although the number of carbon and hydrogen atoms in the ion can be readily established, the question as to which of the hydrogen atoms has separated with a given fragment can only be decided by a study of the mass spectra of isotopically "labelled" compounds[6,7]. Information on the structure of ionised fragments can also be obtained by measuring the energy changes in the reactions that occur and by studying metastable transitions.

All the ions formed in the primary step of interaction of the electrons with the molecule† may be divided into three groups: (1) stable ions, with insufficient excitation energy for decomposition before detection; (2) unstable ions, with sufficient energy for decomposition before they leave the ion source; and (3) metastable ions of intermediate energy[8]. The latter, which decompose after acceleration (but before deflection by the magnetic field), are generally focussed with the production of "false" peaks corresponding to ions of "non-integral" mass. The relationship between the apparent mass of the metastable ion, m^*, the mass of the initial ion before dissociation, m_0, and the mass of the fragmentation ion is expressed by the equation $m^* = m^2/m_0$. The metastable ions are "witnesses" of a given stage of the decomposition process, and they can be used to decide the question of the probable routes of dissociative ionisation.

Temperature is one of the other factors that affect the distribution of intensities in mass spectra. An increase in the temperature of a gas increases the vibrational energy of the molecules and in this way changes the probability of formation of various ions in the mass spectrum of the compound under examination. The most reliable studies on the temperature dependence of mass spectra indicate that there are different changes in intensity of the peaks of various ions[9-12]. The intensity of a molecular-ion peak always decreases with increase in temperature; the peaks of fragmentation ions can increase, decrease, or pass through a maximum; the intensity of ion peaks due to the end products of dissociative ionisation increases with increasing temperature. The value of the complete ionisation depends little, or not at all, on change of temperature.

The variety of phenomena that occur on the interaction of complex molecules with electrons is not limited to those mentioned above. We thought it expedient to consider only those phenomena and characteristics that reflect the specific features of dissociative ionisation processes.

Any examination of the present state of the theory of molecular mass spectrometry from the point of view of the organic chemist must take into account the fact that none of the current views allows quantitative predication of the intensity distribution in the mass spectrum of a complex organic compound of known formula. Therefore, in addition to work designed to set up a quantitative theory of the formation of mass spectra, based on studies of primary and secondary acts in the ionisation of complex molecules, research work is also needed to establish correlations between the structures of organic compounds and their mass spectra. The study of regularities in the mass spectra of organic compounds, and of the relationship between structure and intensity distribution, brings us nearer a solution of the problem of determining a structure from the results of mass-spectrometric analysis. The establishment of different kinds of empirical rules will provide the basis for the development of methods of identification and of qualitative and quantitative analysis.

The methods of molecular mass spectrometry are widely used to study various classes of organic compounds, but their greatest analytical use has been in the hydrocarbon field. However, despite the large number of published papers on the subject, up to now there has been no general systematic summary of the regularities in the mass spectra of hydrocarbons with different degrees of unsaturation. The present review is an attempt, in some measure, to fill this gap.

II. PARAFFIN HYDROCARBONS

The most intense peaks in the mass spectra of hydrocarbons correspond to ions of odd mass number[13] with an even number of electrons, $C_2H_5^+$, $C_3H_7^+$, $C_4H_7^+$, $C_4H_9^+$, etc. The absence from paraffin molecules of groupings that either are stable to electron impact, or produce considerable weakening of certain single bonds, makes it difficult to establish correlations; usually, the primary decomposition process is clear only for branched molecules.

Bloom and coworkers[14], and also Mohler and coworkers[15], studied the mass spectra of octane and nonane isomers and extended the regularities they discovered to all paraffin hydrocarbons. They showed that the most probable processes are those in which the fragmentation ions $C_3H_7^+$ and $C_4H_9^+$ are formed. Molecules with ethyl, propyl, and isopropyl groups readily eliminate these ions, the ion produced corresponding to the mass of the remaining part of the molecule. In most instances, hydrocarbons with a terminal tertiary butyl group give similar spectra, the maximum peak corresponding to $C_4H_9^+$ ions.

In many instances the configuration of the carbon atoms in the hydrocarbon ions can be determined by examining the energetics of the process without the use of labelled compounds[16]. A study of the potentials at which the $C_2H_5^+$, $C_3H_7^+$, and $C_5H_{11}^+$ ions appear‡ in the mass spectra of the normal paraffin hydrocarbons[17] C_5H_{12} and C_8H_{18} has shown that propyl, butyl, and pentyl ions have the secondary structure, but the free radicals formed with them usually have the primary structure, and only sometimes the secondary. The stability of the $C_3H_7^+$ ion, which is encountered in considerable quantities in the mass spectra of all paraffin hydrocarbons, appears to be associated with its cyclopropenyl structure, that is, with the presence of a protonated cyclopropane ring[18]. This conclusion was further supported by the work of Stevenson[7], who established that, in the mass spectra of [1-^{13}C]propane and [2-^{13}C]propane, the relative intensities of the peaks for the fragmentation ions $C_1H_x^+$ and $C_2H_x^+$ are identical; this indicates that the carbon atoms are indistinguishable in the molecular ion $C_3H_8^+$, from which these fragments are formed. Urch also showed that with ionisation by electron impact there is a change in the symmetry of the neutral molecule[19].

Of 80 mass spectra of alicyclic C_2–C_{12} hydrocarbons presented in the catalogue of the American Petroleum Institute[20], only two (those of ethane and 3,4-dimethylhexane) show the formation of more intense peaks of the

† The primary processes also include electron capture and the formation of negative ions. However, since these processes are not typical of hydrocarbons, we shall not consider them here.

‡ The adiabatic ionisation potential of a molecule or atom is theoretically defined as the energy required for the removal of an electron from a neutral particle in the ground state with the formation of a molecular or atomic ion, also in the ground state. The ionisation potential determined by the electron-impact method is, in most instances, the so-called "vertical potential", which exceeds the adiabatic potential by the energy of vibration at excitation of the ion; this is due to the difference in the equilibrium configurations of the nuclei in the molecule and in the molecular ion. The term "appearance potential" applies to those instances of ion formation in which dissociation accompanies ionisation; the appearance potential corresponds to the minimal energy for the production of fragmentation ions.

fragmentation ions $C_2H_4^+$ and $C_4H_8^+$, with an odd number of electrons. Intense peaks of $C_nH_{2n}^+$ ions, the formation of which was related to the elimination of groups with tertiary carbon atoms and the migration of hydrogen, have also been observed in the mass spectra of some dodecanes[21].

The formation of ions which isomerise is not generally typical of paraffin hydrocarbons, but in some instances, for example, in the dissociative ionisation of neohexane, the formation of $C_3H_7^+$ ions must entail rupture of two C–C bonds and migration of a hydrogen atom. These considerations are also valid for the $C_2H_5^+$ ion in the spectrum[22] of isobutane $(CH_3)_3CH$. Analysis of the mass spectra of deuterated hydrocarbons also indicates that migration occurs. For example, $(CH_2D)^+$ and $(CHD_2)^+$ ions are present in the mass spectrum of 1,1,1-trideuteroethane[17].

Several hypotheses have been advanced to explain the specificity of decomposition of complex molecules, including hydrocarbon molecules. An attempt to solve this problem based on the concept of the distribution of the electron density of single bonds[23] led to disagreement with the experimentally observed distribution of intensities, particularly for C_3 and C_4 ions of long-chain molecules[24,25]. Nor were positive results obtained when bond energies for the initial molecule were used to calculate mass spectra; the appearance of very high peaks coreesponding to ions with a small number of carbon atoms could not be explained[26,27].

The quasi-equilibrium theory of mass spectra[28,29] allows the calculation of intensities in the mass spectra of paraffin hydrocarbons containing not more than five carbon atoms. Satisfactory results were obtained in the calculation of mass spectra of low-molecular ethers, alcohols, etc.[30–34] In the investigation of large molecules, a discordance was observed between theory and experiment, particularly in the region where the ionising electrons have low energies; most of the fragments are then formed by direct dissociation on electron impact. The normal paraffins C_nH_{2n+2} from C_6 to C_{30} have been used as models to explain the factors which give rise to the anomalous (from the standpoint of statistical theory) decomposition of molecules on electron impact[35]. Treatment of the mass spectra of these compounds showed that the yield of heavy ions (with the number of carbon atoms in the ion $m \geq 15$) does not depend on m and n as such, but is determined only by $(n - m)$, that is, by the size of the neutral fragment. For low values (3–15) of m, the yield of ions depends on both n and m.

Ryhage and coworkers[36] examined the mass spectra of the labelled paraffin hydrocarbon $CD_3-[CH_2]_{24}-CD_3$ and concluded that fragmentation ions are formed from the central portion of a saturated chain, since the C_2-C_5 fragmentation ions contained no deuterium. Theoretical investigation of the dissociation of molecular ions of normal paraffins has shown[37] that fragmentation ions are formed as a result of competing successive decomposition steps; each ion decomposes in such a way that no charged fragments are formed with less than half the initial number of carbon atoms.

Gur'ev and coworkers[38,39], who studied the mass spectra of [5-^{13}C]-n-nonane, suggested that fragmentation ions are formed by "shedding" of a charged part of the molecule in the region of electron impact, the C–C bonds being ruptured at equal distances from the point of impact. The complete set of probabilities of the mass spectra of an infinitely large molecule appear at each point of collision (independently of the size of the molecule); if the rupture of one of the bonds should take place "outside the limits" of the molecule, only one bond is broken and a smaller fragment is formed. Potapov and coworkers[40,41] studied the probability curves for the appearance of various ions, which give an indication of the mechanism by which ions are formed, and they showed that C_nH_{2n+1} ions are formed from n-octane and n-nonane by simple rupture of one C–C bond to give an ion and a radical. The formation of ions accompanied by the production of many neutral fragments is less favoured energetically. Examination of the mechanism of formation of $C_nH_{2n}^+$ ions, in particular $C_3H_6^+$ ions, led to the conclusion that rupture of two C–C bonds and union of the terminal parts of the hydrocarbon chain take place in a synchronous step. Comparison of the mass spectra obtained in electron and ion collisions[42] showed that dissociation of the ions occurs some time after the moment of excitation, and the relative decomposition probabilities depend to a small extent on mass and type of neutral particle with which collision occurs[43].

To establish the role of different mechanisms for the formation of the commonest ions, $C_3H_7^+$ and $C_4H_9^+$, in the mass spectra of long-chain paraffins, Beynon and coworkers studied [4-^{13}C]-n-eicosane and [1-^{13}C]-n-heptadecane and examined the degree of enrichment of fragmentation ions with heavy carbon[44]. The following hypothetical routes of formation of ions were considered: (1) simple rupture of one carbon–carbon bond in the molecular ion with the formation of an ion and a neutral fragment; (2) rearrangement of the molecular ion to a protonated ring structure; (3) complete "disintegration" of the carbon–carbon skeleton before the formation of fragments; (4) removal of any given number of adjacent carbon atoms from a (linear) molecular ion; (5) decomposition of a molecular ion with simple rupture of the carbon–carbon double bond, followed by rearrangement of the fragmentation ion to a ring structure and further fragmentation by Scheme (2); (6) simple bond rupture with subsequent removal of C_2H_4 fragments.

The validity of these hypotheses was tested by comparing experimental and calculated curves reflecting the proportion of unlabelled and labelled fragmentation ions with a different number of carbon atoms. The results showed that ions with a small number of carbon atoms are generally not formed by simple rupture of the carbon chain. On the other hand, rupture of one C–C bond is characteristic for larger ions. Further decomposition occurs mainly by successive removal of C_2 ions. The hypothesis that a ring structure is formed directly from a molecular ion is not in agreement with experimental results obtained with heavy fragments. The best agreement between the experimental and theoretical curves was obtained with mechanism (5); it was assumed, from steric considerations, that the rings usually contain five or six carbon atoms.

The specificity of dissociative ionisation of paraffins with a normal, or not too branched, chain is reflected in the nature of the distribution curve: the maximum corresponds to $C_3H_x^+$ ions, which are formed with the highest probability, irrespective of the length of the paraffin chain (Fig. 1). When the chain contains quaternary carbon atoms, a second maximum appears. Thus, investigation of the mass spectra of isomeric tetradecanes with the methyl side group in different positions showed that secondary maxima appear, owing to the rupture of a bond at the tertiary carbon atom[45,46].

The degree of decomposition of the paraffin molecule that occurs when it interacts with ionising electrons depends

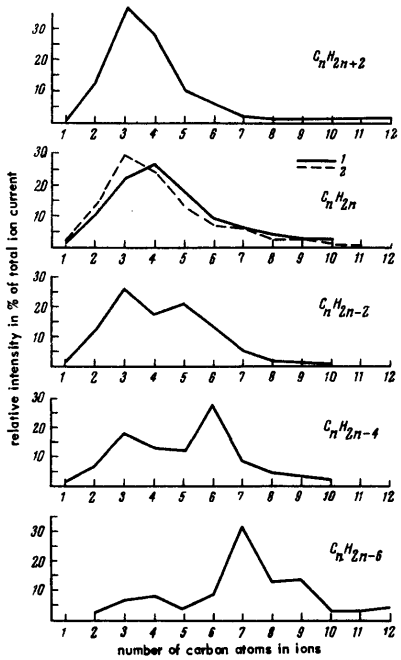


Fig. 1. Distribution curves of intensities against number of carbon atoms in ions for different hydrocarbon groups
1) naphthene; 2) monoalkene.

on the branching of the carbon skeleton: Bloom and coworkers analysed the spectra of 18 octane isomers and showed that the most intense molecular-ion peak is observed in the mass spectrum of the normal isomer[14]. Examination of the spectra of the tetradecanes[45,46] and the hexadecanes[47] showed a similar picture. The intensity of the molecular-ion peak decreases with increase in molecular weight; a more rapid rate of decrease is shown by branched paraffins than by the normal isomers. The peak intensities of the molecular ions of C_6–C_{12} hydrocarbons are, with some exceptions, 3–6% of the maximum. Further increase in molecular weight leads to virtually complete disappearance of the molecular-ion peaks in the spectra of branched paraffins[48]. Gur'ev examined the mass spectra of normal paraffins and showed that the dependence of the fraction of molecular ions on molecular size is well represented by an exponential curve[49]. Polyakova and coworkers[50] studied the mass spectra of normal paraffins on different instruments, and showed that, in all instances, the sensitivity coefficients of the molecular-ion peaks are a function of molecular weight. However, the nature of the dependence, which is represented by an interpolation formula, varies somewhat from one instrument to another.

III. NAPHTHENE HYDROCARBONS

In many ways the dissociative ionisation of naphthene hydrocarbons is similar to the process observed when electrons interact with paraffin molecules.

Unlike paraffins, naphthene hydrocarbons have intense molecular-ion peaks; for C_6–C_{11} isomers, the mean intensity of the molecular-ion peaks is 18.5% of the maximum.

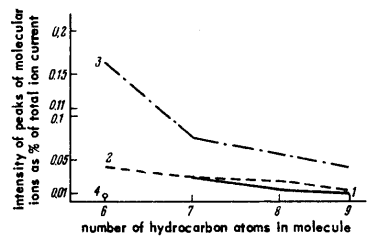


Fig. 2. Stability of $C_nH_{2n}^+$ molecular ions to electron impact:
1) monoalkenes; 2) five-membered naphthenes; 3) six-membered naphthenes; 4) ethylcyclobutane.

The stability of naphthene hydrocarbons to electron impact is greater than that of paraffins, and it does not change so sharply as the number of carbon atoms in the molecule increases. However, hydrocarbons with the empirical formula C_nH_{2n} differ in their resistance to electron impact. Fig. 2 shows the intensities of the molecular-ion peaks relative to the complete ion current in the mass spectra of monoalkenes and naphthene hydrocarbons with five- and six-membered rings. The figures representing the degree of decomposition of monoalkenes and cyclopentane hydrocarbons are very close (curves *1* and *2*), but the figures for cyclohexane hydrocarbons (curve *3*) indicate that these are much more stable to electron impact.

Several qualitative relationships between the structure of the initial molecule and the intensity of the molecular-ion peaks in the mass spectra of naphthene hydrocarbons can be established: (1) the molecular peaks of hydrocarbons with a five-membered ring are, as a rule, less intense than the corresponding peaks of naphthenes with a six-membered ring; (2) *gem*-disubstituted hydrocarbons have the lowest molecular peaks; (3) with few exceptions, hydrocarbons with a branched group attached to the ring have a lower molecular peak than hydrocarbons with an unbranched group having the same number of carbon atoms.

In comparison with paraffins the dissociative ionisation of naphthene hydrocarbons is associated with a much greater probability of processes in which a hydrogen atom migrates. As a result, so-called "pseudomolecular" fragmentation ions are produced with the same mass as true molecular ions from a homologue of lower molecular weight.

Stevenson[51], who studied the mass spectra of five-membered naphthene hydrocarbons, showed that, under electron impact, the excited molecular ion rearranges to the corresponding alkene ion, which undergoes further dissociation. For example, when methylcyclopentane labelled with ^{13}C dissociates, the methyl group is not removed directly, but a number of successive reactions occur that lead to the formation of methyl and other, heavier fragmentation ions. Energy calculations also show that $C_5H_9^+$ ions, which are formed by the decomposition of cyclopentane hydrocarbons, correspond to alkenes with some excess energy[52]. Analysis of the mass spectra of labelled cyclohexane, methylcyclohexane, ethylcyclopentane, and methylcyclopentane[53] has shown that, for methylcyclopentane, the ^{13}C atom may appear on the $C_5H_9^+$ or the CH_3^+ ions with equal probability; consequently, on ionisation the ring is ruptured at the substituent and the open chain then dissociates.

With methylcyclohexane, the CH_3 group is removed only from the side-chain. CH_3 and C_2H_5 groups removed from molecular ions of ethylcyclopentane and methylcyclopentane are only partly derived from the side-chain. With methylcyclohexane and methylcyclopentane, C_2H_4 groups are detached mainly from the ring, and with ethylcyclopentane exclusively from the ring. The heats of formation of $C_6H_{11}^+$ ions from cyclohexane and methylcyclohexane undoubtedly show that dissociative ionisation of hydrocarbons of this type gives an ion with a cyclic and not the alkene structure which occurs with cyclopentane hydrocarbons. The differences in behaviour of cyclopentane and cyclohexane hydrocarbons on electron impact is in accord with the stereochemistry of alicyclic compounds[54]. The presence of CH_3^+ ions in the mass spectrum of cyclobutane also points to the possibility of isomerisation to a structure of the type $(CH_3-CH-CH_2-CH_2)^+$,[55] the formation of which is associated with ring cleavage and migration of a hydrogen atom to one of the end carbon atoms. The likelihood of this process has been confirmed by a study of deuterated cyclobutane. Isomerisation of the molecular ion of naphthene hydrocarbons competes with the process in which two bonds of the naphthene ring are ruptured and a stable radical or molecule is formed, and possibly also with the process in which a group attached to the ring is removed. The probability of these processes depends on the structure of the ring and on the nature of the substituent[56-58].

The effect of stereoisomerism on the distribution of intensities in mass spectra was observed in a study of 1,2-, 1,3-, and 1,4-dimethyl cyclohexanes[59,60]. The spectra of the *cis*- and *trans*-isomers differed materially in the number of $(M - 15)^+$ ions§. Thus, the probability of removal of a methyl group from 1,2-dimethylcyclohexane was 35% greater for the *trans*-isomers; with 1,3-dimethylcyclohexane, it was 20% greater for the *cis*-isomer; and with 1,4-dimethylcyclohexane, it was 7% greater for the *trans*-isomer.

Special features in the molecular structure of naphthene hydrocarbons are also reflected in the distribution curve of ion intensities according to the number of carbon atoms[61]. In the dissociative ionisation of five- and six-membered naphthene hydrocarbons, roughly equal amounts of $C_3H_x^+$ and $C_4H_x^+$ ions are formed, but the amount of $C_5H_x^+$ ions formed differs significantly; the proportion of these ions formed from cyclopentane hydrocarbons is 2 to 2.4 times that formed from cyclohexane hydrocarbons

IV. MONOALKENE HYDROCARBONS

The interpretation of the mass spectra of monoalkene hydrocarbons is very complicated. The probability of the decomposition of paraffin hydrocarbons is mainly determined by the size of the molecule and the nature of the branching, but the direction of dissociative ionisation of monoalkene hydrocarbons is affected by the position of the double bond and by its interaction with nucleophilic methyl groups.

The increased resistance to electron impact of monoalkene molecules compared with alkanes means that in the mass spectra of monoalkenes the molecular ions give fairly intense peaks. The intensities for C_6-C_{12} hydrocarbons vary, as a rule, between 20% and 30% of the maximal peak, and sometimes they may even exceed 40%; only a small number of isomers have molecular-ion peaks with intensities less than 10% of the maximal.

The most intense peaks of fragmentation ions in the spectra of monoalkenes are formed, as a rule, by the rupture of the bond in the β-position to the double bond. The probability of this process increases when one or two methyl groups are attached to the carbon atom in the α--position to the double bond, and when a hydrogen atom migrates. Rupture of the bond in the α-position to the double bond, which is frequently accompanied by migration of a hydrogen atom, competes with this process. A double bond nearer the centre of the molecule is more likely to undergo decomposition[62]. However, in this case decomposition also occurs at the β-bond; two decomposition routes are therefore possible, and the predominance of one over the other is determined by the presence or absence of branching and by the position of the branching when it is present.

The migration of hydrogen is of great importance in the dissociative ionisation of monoalkenes; this migration leads to the formation of "pseudomolecular" ions, which are identical with molecular ions of lower members of the homologous series.

The formation of $(M - 15)^+$ ions is also typical, particularly in those instances in which the methyl group is attached at the β-position to the multiple bond. Thus, this process leads to the formation of an intense $C_5H_9^+$ peak (91.3% of the maximal) in the spectrum of 4-methylpent-2--ene. The probability of removing a methyl group is increased when several methyl groups are in the β-position to the double bond.

The intensity of ion peaks associated with rupture of the β-bond largely depends on the structure of the alkyl group and can be evaluated quantitatively in some instances. The results of calculations presented in Fig. 3 show that the probability of forming ions of mass 57 is about 6 times as great for the tertiary butyl group as for the normal butyl group. When the butyl group is in the α-position to the double bond, the peak intensity of ions of mass 57 sharply decreases. However, as for β-bond rupture, the greatest intensity is shown by the ion peak corresponding to a charged group with a tertiary carbon atom.

The same regularities have been established (less clearly, however) for hydrocarbons containing propyl and isopropyl groups. The maximal peaks corresponding to removal and formation of the $C_3H_7^+$ ion are associated with a structure containing this ion in the β-position to the double bond. The dependence of the intensity of ions of mass 43 on the structure of the propyl group and its position relative to the double bond is illustrated by the graph in Fig. 3. Normal alk-1-enes that form "paraffin-type" fragments in considerable quantity, and in particular, fragments corresponding to ions of mass 43, have not been considered.

The selectivity of dissociative ionisation of monoalkenes is reflected not only in the preferential formation of $C_nH_{2n-1}^+$ ions but also in the distribution of intensities according to the number of carbon atoms in the ions. The nature of the distribution curves is related to differences in the molecular structure of the isomers and depends on the position of the double bond in the structure of the carbon skeleton[63]. Alkenes with a normal carbon chain (Fig. 4) have one maximum on the distribution curve, corresponding to $C_3H_x^+$ ions for alk-1-enes and -3-enes, and to $C_4H_x^+$ ions for alk-2-enes and -4-enes. The shape of

§ M denotes the mass of the molecular ion.

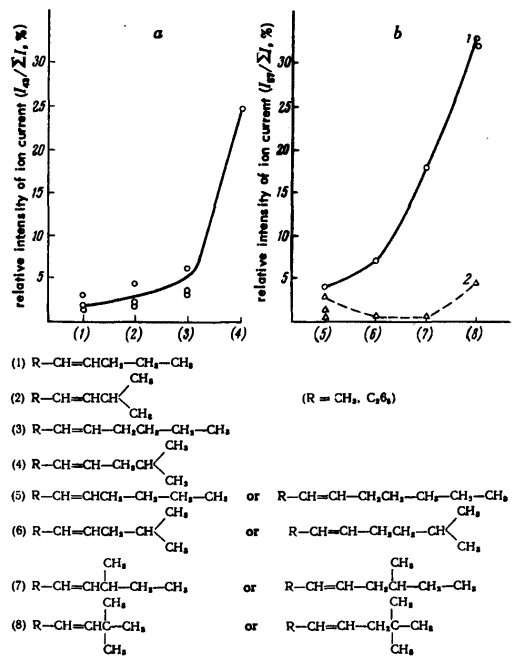


Fig. 3. Effect of structure and position of alkyl group on intensity of formation of ions of mass 43 (*a*) and 57 (*b*):
1) rupture of β-bond; 2) rupture of α-bond.

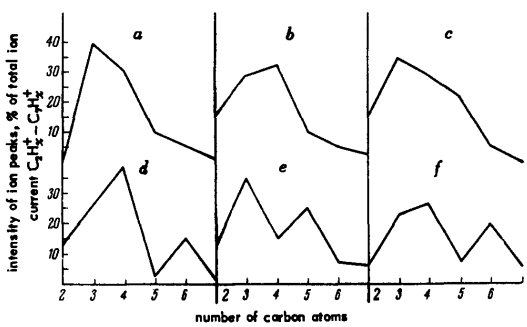


Fig. 4. Distribution of intensities against number of carbon atoms in ions for different types of monoalkenes.

the distribution curve changes as the degree of branching of the carbon skeleton increases; the formation of about equal amounts of $C_3H_x^+$, $C_4H_x^+$, and $C_5H_x^+$ ions is characteristic of mono- and di-substituted alk-1-enes (Fig. 4*c*). In addition to a maximum for $C_4H_x^+$ ions, the distribution curves of trimethylalk-1-enes show a second maximum, corresponding to $C_6H_x^+$ ions. Monomethylalk-2-enes and -3-enes show two maxima, $C_3H_x^+$ and $C_5H_x^+$. The maxima of dimethyl- and trimethylalk-2-enes correspond to $C_4H_x^+$ and $C_6H_x^+$ ions.

For a long time it was accepted that geometric isomerism of monoalkenes had no effect on the nature of the mass spectrum[64,65]. Later work showed the possibility of identifying *cis*- and *trans*-butylenes[66]. Investigation of geometric isomers showed that the differences in the mass spectra of isomers become more marked as the ionising energy of the electrons decreases, because near the ionisation threshold the greater internal energy of the *cis*-isomers compared with the *trans*-isomers facilitates dissociation[67]. This is confirmed by the values of the ionisation potentials, which are lower for the *trans*-isomers than for the *cis*-isomers[68]. Similar conclusions can be drawn from the work of Natalis[69], who showed that, when monoalkenes of the type R–CH=CHR′ (where R and R′ are methyl, ethyl, secondary propyl, or t-butyl groups), the ratio of the intensities of the molecular-ion peaks for *trans*- and *cis*-isomers increases as the size of the group increases[69]. This effect is due to liberation of excess energy on isomerisation of the *cis*-isomer with a larger alkyl radical, which promotes more rapid decomposition of the ion formed.

Arbuzov and coworkers[70] studied the mass spectra of Δ^3-carene oxide (α- and β-forms), camphene oxide, and β-pinene oxide at electron-ionising energies of 50 and 9 eV, and showed that stereoisomerism has an important effect on the course of dissociative isomerisation of these molecules, changing the probability of even very "energy-consuming" processes.

Using an MX1304 mass spectrometer, the authors studied the mass spectra of the *cis*- and *trans*-isomers of pent-2-ene: at 70 eV the distribution curves for both isomers are virtually identical; at 20 eV the quantity of ions containing five carbon atoms is about 20% greater for *trans*-pent-2-ene than for *cis*-pent-2-ene, which allows identification of these isomers.

The problem of the probability of rupture of the C–H bond has been considered[71,72]. When ethylene is ionised by monochromatised electrons, $C_2H_3^+$ ions are formed; the considerable yield of ions in this process is due to the relatively low ionisation potential of the C_2H_3 radical (9.55 eV). Study of the mass spectra of molecules of propene and its deuterated derivatives, CH_2CHCH_3, CH_3CDCH_2, CH_3CHCD_2, and CD_3CHCH_2, has shown that $C_3H_5^+$ ions are formed with equal probability from propene and from CH_3CDCH_2. Thus, in dissociative ionisation the C–H (or C–D) bond is ruptured at the central carbon atom. To elucidate the mechanism of dissociative ionisation of ethylene, the mass spectra of this compound were investigated at electron energies of 10–70 eV; tetrafluoroethylene was examined in the same way[73]. It is suggested that a number of peculiarities in the mass spectra may be explained by a difference in charge distribution in molecular ions.

V. UNSATURATED C_nH_{2n-2} HYDROCARBONS

All hydrocarbons of this group with a normal carbon skeleton readily ionise on electron impact. Conjugated diene hydrocarbons are somewhat more stable. Complete ionisation is little affected by the mutual arrangement of the multiple bonds; different isomers form about the same number of ions per unit quantity of compound[14].

The structure of the carbon skeleton, in combination with the position of the multiple bonds, has a much greater effect on the character of the distribution of the ion intensities in the mass spectrum.

1. 2,3- and 3,4-Diene Hydrocarbons

In the mass spectra of 3,4-dienes (octa-3,4-diene, 7-methylocta-3,4-diene, deca-3,4-diene[74]), the greatest

intensity is shown by the peak of $C_5H_7^+$ ions, which are formed on rupture of the bond in the α-position to the allene group, accompanied by elimination of a larger group. In addition, the excited molecular ion decomposes simultaneously at two C–C bonds with the formation of $C_3H_x^+$ ions. Of the ions of this type, the most intense are $C_3H_3^+$ and $C_3H_5^+$, that is, those ions with a conjugated or a cyclopropenyl structure[22].

The general nature of mass spectra of 2,3-dienes is similar to that of 3,4-dienes; the curve showing the distribution of intensity against the number of carbon atoms in the ions also has two maxima, corresponding to the $C_3H_x^+$ and $C_5H_x^+$ ions. However, the maximal intensity in the spectrum is shown not by the peak of $C_5H_7^+$ ions but by the peak of $C_5H_8^+$ ions, which are formed by decomposition of a molecular ion at the β-bond, accompanied by migration of hydrogen.

Some information on the mechanism of formation of the most intense ions in the spectrum can be obtained by examining the curves showing the effectiveness of ionisation¶. Curves for the probability of appearance of ions of mass 67, which are of maximal intensity in the spectrum of 3,4-dienes, show that changes in the intensity of the ion current as a function of electron energy can be represented virtually by a single general curve[74]; this appears to indicate that this ion is formed by the same mechanism from different 3,4-dienes. For octa-3,4-diene, 7-methylocta-3,4-diene, and deca-3,4-diene, the appearance potentials are within the range 11.6–11.9 eV. The appearance potentials of ions of mass 68, corresponding to the maximal peaks in the spectra of octa-2,3-diene and 7-methylocta-2,3-diene, are 9.2 and 9.9 eV respectively. The appearance potentials of ions of mass 67 are considerably higher, at 13.8 and 12.7 eV.[74] It would appear that the penta-1,3-diene structure can be ascribed to $C_5H_8^+$ ions formed by rupture of a β-bond accompanied by migration of hydrogen. This hypothesis is confirmed by the values of the heats of formation — 9.64 eV for the penta-1,3-diene molecular ion, and 9.68 eV for $C_5H_8^+$ ions.

The mass spectrum of 7,7-dimethylocta-3,4-diene differs markedly from the spectra of other representatives of this series[74]; its intensity distribution curve shows only one maximum, corresponding to $C_4H_x^+$ ions. The peak of $C_4H_9^+$ ions shows the maximal intensity. An explanation of the anomalous dissociation of 7,7-dimethylocta-3,4-diene is probably to be sought in the different ways various atomic groupings can affect the electron-density distribution in the molecule. The ease with which the $C_4H_9^+$ ion is formed may be due to polarisation of the C–C bond on interaction with electrons of a molecule containing a tertiary butyl group. The formation of a tertiary butyl ion is favoured by energy considerations, since the corresponding decomposition of the initial molecular ion is either exothermic or thermoneutral. Similar specificity in the decomposition of 7,7-dimethylocta-3,4-diene is in agreement with the known relationship[75], according to which the extent of removal of alkyl groups on electron impact increases linearly in the sequence: normal, iso-, and tertiary alkyl groups. This tendency, which is more pronounced in compounds with a permanent dipole, can also be traced in the

¶ In determinations on the mass spectrometer of ionisation and appearance potentials, the change in ion current is recorded as a function of the energy of the ionising electrons; what is termed an ionisation effectiveness or probability curve is then obtained, from which the ionisation potential is determined by some method.

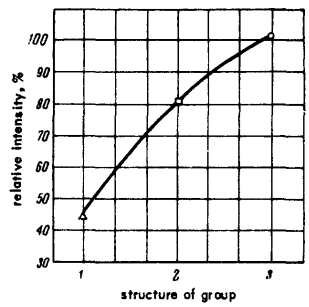


Fig. 5. Probability of decomposition at β-bond in 3,4-diene hydrocarbons:
1) normal structure; 2) iso-structure;
3) tertiary.

3,4-diene series. When a β-bond in 7,7-dimethylocta-3,4-diene is broken, $C_4H_x^+$ ions are formed. When the same bond is broken in 7-methylocta-3,4-diene, $C_3H_x^+$ and $C_2H_x^+$ ions are formed. Fig. 5 shows how the decomposition probability changes from the normal to the tertiary alkyl group. The $C_4H_9^+$ ion, which has the greatest probability of formation in the mass spectrum of 7,7-dimethylocta-3,4-diene shows the lowest appearance potential, 11.7 eV, in comparison with the ions $C_3H_5^+$, $C_3H_7^+$, and $C_5H_8^+$, for which the potentials are 15.0, 13.5, and 12.6 eV respectively.

Investigation of the mass spectra of 2,2-dimethyldeca-3,4-diene, 2,2,7,7-tetramethylocta-3,4-diene, and 4,4-dimethylpent-1-ene has permitted elucidation of the effect on dissociative ionisation of the structure of the butyl group at the β-carbon atom[76]. In the mass spectra of these hydrocarbons, the greatest intensity is shown by ion peaks formed by decomposition of a molecular ion into a butyl radical and a fragmentation ion containing multiple bonds. For 2,2-dimethyldeca-3,4-diene and 2,2,7,7-tetramethylocta-3,4-diene, the relevant ions are $C_4H_9^+$ and $C_8H_{13}^+$; for 7,7-dimethylocta-3,4-diene, $C_4H_9^+$ and $C_6H_9^+$; and for 4,4-dimethylpent-1-ene, $C_4H_9^+$ and $C_3H_7^+$. The $C_4H_9^+$ ion evidently corresponds to the butyl group in the β-position to the double bond. The probability of forming this ion, which is determined by the structure of the group, can be characterised by the ratio of the height of the $C_4H_9^+$-ion peak to the full ion current and by the dependence of this quantity on the relative weight of the tertiary butyl group in the molecule (Fig. 6). The intensity of formation of the $C_4H_9^+$ ion is a linear function of the relative weight of the t-butyl group (in the β-position to the double bond) in the molecule. It is noteworthy that the monoalkenes are also subject to this relationship (point *4* on Fig. 6). The probability that a positive charge will be found on one of the two fragments formed when the molecular ion decomposes is determined by the structure of the butyl group. The greater the relative weight of the tertiary butyl group, the greater will be the intensity of the peak of the $C_4H_9^+$ ion in comparison with the $(M - 57)^+$ ion. Thus, for 2,2,7,7-tetramethylocta-3,4-diene and 7,7-dimethylocta-3,4-diene, dissociative ionisation proceeds mainly with rupture of the β-bond between the t-butyl group and the allene grouping to give the ions $C_4H_9^+$, $C_8H_{13}^+$, and $C_6H_9^+$ respectively. The two latter ions appear to serve as sources of ions of mass 95, 81, 67, and 39, which are formed by elimination of methylene radicals. In the mass spectra of 2,2-dimethyldeca-3,4-diene, successive decomposition processes, together with rearrangements, play a much more important part than does rupture

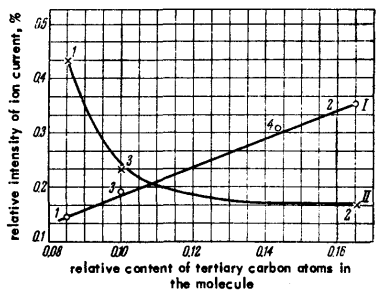


Fig. 6. Relationship between the structure of the butyl groups and the probability of formation of $C_4H_9^+$ ions. I) $I_{57}/\Sigma I_j$; II) I_{57}/I ($M = 57$): 1) 2,2-dimethyldeca-3,4-diene; 2) 2,2,7,7-tetramethylocta-3,4-diene; 3) 7,7-dimethylocta-3,4-diene; 4) dimethylpent-1-ene.

of the $C_4H_9-C_8H_{13}$ bond. The peaks of rearrangement ions of empirical formula C_nH_{2n-2} are very intense; the ions $C_5H_8^+$, $C_6H_{10}^+$ and $C_8H_{14}^+$ are stabilised with the migration of hydrogen. When the electron-ionising energy is reduced from 70 to 20 eV, the selectivity of decomposition greatly increases, and the quantitative ratio of the characteristic ions changes somewhat. In the mass spectrum of 2,2-dimethyldeca-3,4-diene, at electron energies of 70 eV, the probability of finding a positive charge on the $C_4H_x^+$ ions was 2.6 times greater than that for $C_8H_x^+$ ions. At 50 eV these values are fairly close, and at 20 eV the intensity of $C_8H_x^+$ ions is 1.6 times that of $C_4H_x^+$ ions. For 2,2,7,7-tetramethylocta-3,4-diene, reduction of the electron-ionising energy from 70 to 30 eV leads to a relative increase in the number of $C_8H_x^+$ ions compared with the number of $C_4H_x^+$ ions, but the intensity of the latter changes very little.

The structure of the $C_4H_9^+$ ions formed in the dissociative ionisation of the β-bond in 2,2-dimethyldeca-3,4-diene and 2,2,7,7-tetramethylocta-3,4-diene can be deduced by comparing the heats of formation of these compounds[76]. The $C_4H_9^+$ ions must obviously have a different structure, while the C_8H_{13} radicals are probably identical.

The heats of formation† of $C_8H_{13}^+$ ions were 9.10 and 9.00 eV. This suggested that the C_8H_{13} radicals produced when $C_4H_9^+$ ions are formed have the same heats of formation. It thus become possible to evaluate the difference in heats of formation of $C_4H_9^+$ ions, which was found to be 0.55 eV. A similar difference (0.56 eV) was observed in the heats of formation of the $C_4H_9^+$ ions produced by dissociative ionisation of iso- and n-butanes[78]. The existence of this difference shows that the $C_4H_9^+$ ions formed by electron impact differ in structure from one another in the same way as the groups forming part of the molecule under examination.

2. Conjugated Dienes

On electron impact, conjugated diene hydrocarbons with a normal or slightly branched chain of carbon atoms behave in the same way as alkenes and mainly from $C_3H_x^+$ and $C_5H_x^+$ ions. The mass spectra of conjugated diene hydrocarbons with a t-alkyl group at the double bond, such as:

$(CH_3)_3C-CH=CH-CH=CH_2$	(C_8H_{14})
$(CH_3)_2(C_2H_5)C-CH=CH-CH=CH_2$	(C_9H_{16})
$(CH_3)(C_2H_5)_2C-CH=CH-CH=CH_2$	$(C_{10}H_{18})$
$(C_2H_5)_3C-CH=CH-CH=CH_2$	$(C_{11}H_{20})$

are different[79].

In this series of compounds, stability to electron impact decreases with increase in molecular weight; the intensity of the molecular-ion peak decreases by a factor of 5 when the number of carbon atoms in the molecule increases from 8 to 11. Complete ionisation is also a function of molecular weight and increases from 1.18 for C_8H_{14} to 2.74 for $C_{11}H_{20}$‡. A similar dependence was also observed with other types of hydrocarbons[80].

The main decomposition routes of molecular ions are similar for the hydrocarbons that have been examined, but the intensity of fragmentation ions depends on the ratio of methyl and ethyl groups near the tertiary carbon atom. In dissociative ionisation, alkyl or alkenyl groups, or ethylene molecules, are successively eliminated. At first, a methyl group (from C_8H_{14}), or an ethyl group (from other hydrocarbons) appears to be removed from the molecular ion. The maximal intensity in the mass spectra of the hydrocarbons C_8H_{14}, C_9H_{16}, and $C_{10}H_{18}$ is shown by the peaks of ions of mass 95, 109, and 123, that is, $(M-15)^+$ and $(M-29)^+$. These ions can decompose in turn to form smaller fragments. In the dissociation of $C_{11}H_{20}^+$, an ethyl group is eliminated and an ion of mass 123 is formed, which on further decomposition gives an ion of mass 81, corresponding to the maximal peak in the spectrum. The scheme in Fig. 7 illustrates the suggested routes of dissociative ionisation. This sequence of decomposition reactions has been confirmed by the presence of metastable ions.

VI. UNSATURATED C_nH_{2n-4} HYDROCARBONS

This homologous series includes enyne and triene hydrocarbons containing conjugates and unconjugated double and triple bonds[81,82].

The first member of the enyne series, vinylacetylene, is highly resistant to electron impact. The molecular-ion peak shows the greatest intensity in the mass spectrum of this compound. The most abundant fragmentation ions are formed by rupture of the C–H bond. Fragmentation ions produced by decomposition at the carbon–carbon bond are not characteristic of vinylacetylene. Appreciable decomposition at this bond only occurs when an ion of mass 26 is formed.

The introduction of a methyl group into the vinylacetylene molecule at any position somewhat lowers the stability of the molecular ion, but this ion retains its maximal intensity. Thus, the probability of decomposition of vinylacetylene is 60%, compared with 80% for methylvinylacetylene, isopropenylacetylene, and n-propenylacetylene. The probability of rupture of the molecule at a C–H bond is very high and about equal for all isomers, probably because of the formation of ions of mass 65, stabilised by conjugation. Normal hydrocarbons differ from isopropenylacetylene in showing a much more intense peak for ions of

† The heats of formation of allene hydrocarbons were calculated on the basis of the additivity of the thermodynamic functions of the structural groupings that make up the molecule[77].

‡ Complete ionisation was determined relative to benzene.

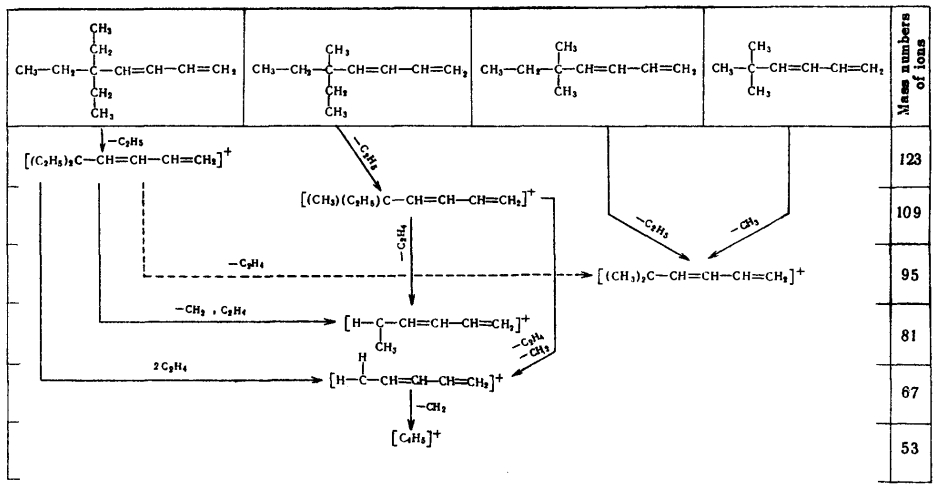


Fig. 7. Scheme of dissociative ionisation of diene hydrocarbons with a tertiary alkyl group at the multiple bond. The dotted line indicates decomposition routes not confirmed by metastable transitions. The figures correspond to the masses of the fragmentation ions.

mass 63. These ions may be produced by the following scheme:

$$C_5H_6^+ \rightarrow C_5H_5^+ \rightarrow C_3H_3^+ + (H_2).$$

Decomposition of the molecule at the bond between the methyl group and the vinylacetylene system occurs to a small extent (15–25%) with all isomers except propynylacetylene. The spectra of all the isomers show a very intense ion of mass 39, the appearance of which is due to rupture of a single C–C bond and loss of hydrogen:

$$C_5H_6^+ \rightarrow C_3H_5^+ \rightarrow C_3H_3^+.$$

The $C_3H_3^+$ ion may also be produced when a molecule decomposes at the triple bond, but its appearance in the spectrum of the branched-chain isomer, and also in the spectra of piperylene and isoprene, indicates that the first hypothesis is more likely to be correct. Examination of the spectra of the methyl derivatives of vinylacetylene shows that introduction of a methyl group adjacent to the triple bond is the factor that has the greatest effect on the stability of the molecular ion.

Investigation of the mass spectra of alkyl derivatives of vinylacetylene of higher molecular weight(pent-1-en-3-yne, hex-1-en-3-yne, oct-1-en-3-yne, and dec-1-en-3-yne) shows[82] that, as the size of the alkyl group increases, the intensity of the molecular-ion peak falls to 1.9% (in the spectrum of dec-1-en-3-yne), but the probability of decomposition increases to 99.5%. The preferential formation of two types of ions, $C_3H_x^+$ and $C_6H_x^+$ is characteristic of all the representatives of the alkylvinylacetylenes studies; these ions correspond to two maxima on the intensity distribution curves of the ions. The $C_3H_3^+$ ions appear to be formed by different mechanisms; in vinylmethylacetylene the ion of mass 39 is produced by simple rupture of a C–C bond, but for other homologues the formation of this ion is associated with the rupture of other carbon–carbon bonds of different stability and with the migration of hydrogen. This hypothesis is confirmed by the values of the appearance potential of the $C_3H_3^+$ ion[82], which are directly proportional to the size of the alkyl radical and vary from 13.0 for vinylmethylacetylene to 18.4 eV for vinylhexylacetylene. The mass spectra of vinylacetylene shows considerable abundance of ions of the type $C_nH_{2n-5}^+$, $C_nH_{2n-7}^+$, and $C_nH_{2n-4}^+$; these are produced by rearrangements in which hydrogen migrates. A specific feature of dissociation, due to the presence of conjugated bonds in the molecule, is that the carbon–carbon bond in the γ-position to the conjugated system in molecules of higher vinylacetylene homologues is the most stable to electron impact. In thermal conversions the β-bond is the least stable.

The introduction of the t-butyl group as a substituent at the double or triple bond in enyne hydrocarbons(2,2-dimethylhex-5-en-3-yne, 2-t-butylbut-1-en-3-yne, 2,2,5-trimethylhex-5-en-3-yne, 2,2-dimethylhept-6-en-3-yne, and 2-t-butylhex-1-en-3-yne)[83] materially alters the intensity distribution of the ions in the mass spectra.

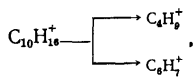
The maximum for $C_3H_x^+$ ions is less sharp because of more intense formation of $C_4H_x^+$ ions, and the maximum for $C_6H_x^+$ ions is affected by the intense formation of $C_7H_x^+$ ions. The maximal peaks in the mass spectra of C_8H_{12} and C_9H_{14} hydrocarbons correspond to ions that are produced by elimination of one methyl group from the molecular ion. This process leads to the formation of $C_7H_9^+$ ions from C_8H_{12} hydrocarbons, and $C_8H_{11}^+$ ions from C_9H_{14} hydrocarbons. In addition, an important part is played by reactions in which hydrogen and methylene groups are eliminated; as a result, the ions $C_7H_7^+$, $C_8H_8^+$, $C_6H_5^+$, etc. appear in the spectra.

The observed analogies suggest the existence of a general mechanism for the formation of fragmentation ions; this may be represented by the following scheme, which includes all ions with an intensity greater than 20% of the maximal:

$$C_8H_{12}^+ \xrightarrow{-CH_3} C_7H_9^+(100\%) \xrightarrow{-2H} C_7H_7^+(50\%) \xrightarrow{-C_2H_2} C_5H_5^+(20\%) \xrightarrow{-C_2H_2} C_3H_3^+(40\text{–}90\%),$$
$$C_7H_7^+ \xrightarrow{-CH_2} C_6H_5^+(75\%) \xrightarrow{-C_2H_2} C_4H_3^+(30\%)$$

$$C_9H_{14}^+ \xrightarrow{-CH_3} C_8H_{11}^+(100\%) \xrightarrow{-2H} C_8H_9^+(25\%) \xrightarrow{-CH_2} C_7H_7^+(30\text{–}90\%) \xrightarrow{-C_2H_2} C_5H_5^+(25\%),$$
$$C_7H_7^+ \xrightarrow{-CH_2} C_6H_5^+(25\text{–}45\%)$$

It follows from this scheme that the formation of $C_4H_9^+$ ions plays an important part only for compounds containing a t-butyl group at the double bond in the β-position to the triple bond; elimination of the t-butyl group is then favoured by the presence of an alkyl substituent in the acetylene grouping. The intensities of the peaks of $C_4H_9^+$ ions in the spectrum of 2-t-butylbut-1-en-3-yne (C_8H_{12}) and 2-t-butylhex-1-en-3-yne ($C_{10}H_{16}$) are 38.2 and 99.6% respectively. Decomposition of the latter compound may be represented as follows:



Any of the fragments formed may carry a positive charge with equal probability. Some stages of the hypothetical successive reactions have been confirmed by the presence of metastable ions in the peaks of the mass spectra. Thus, the mass spectrum of

$$(CH_3)_3C{-}C \equiv C{-}CH_2{-}CH{=}CH_2,$$

indicates the presence of an ion with an apparent mass of 46.6; this corresponds to the following reaction:

$$C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2.$$

Similar processes have also been observed in the dissociative ionisation of alkylbenzenes[84,85,86], cycloheptatriene[87], and spiro[2,4]cycloheptadiene[88]. Ions of mass 91 have been assigned the cyclic tropylium structure, the decomposition of which has been shown by mass spectra of samples labelled with ^{13}C and by energy calculations, to occur by the successive elimination of acetylene molecules.

Definite conclusions on the reactivity of organic compounds can be drawn from a comparison of the ionisation potentials for molecular ion formation. Vinylacetylene (9.9 eV) and isopropenylacetylene (10.1 eV) are the most difficult to ionise. Lengthening of the normal carbon chain adjacent to the triple bond reduces the ionisation potential to 9.4 eV (vinylmethylacetylene), and adjacent to the double bond, to 8.5 eV (propenylacetylene). Thus, the ionisation potentials of molecules change according to the position of the methyl group. It would be interesting to compare these results with those on the kinetics of reactions of vinylacetylenes that proceed by an ionic mechanism. However, information of this kind is not available in the literature.

VII. HYDROCARBONS OF THE GENERAL FORMULA C_nH_{2n-6}

This group includes hydrocarbons with an open chain containing conjugated and unconjugated double and triple bond, cyclic dienes with an unsaturated alkyl group in the side-chain, as well as benzene and its homologues.

Generally, isomeric hydrocarbons show a similar distribution of intensities in their mass spectra. However, the spectra of initial representatives of homologous series of highly unsaturated hydrocarbons, such as the C_nH_{2n-6} series, show considerable differences, which are associated with structural features[89]. In the first place, the stability of the molecule to electron impact varies in the same way as do, for example, the stabilities of the isomeric C_5H_6 enyne hydrocarbons. In the mass spectra of hexa-1,3-diyne, hexa-2,4-diyne, hexa-1,5-dien-3-yne, and benzene, the relative stability of the molecule, in the same way as the full ion current, depends largely on the structure of the initial C_6H_6 hydrocarbon. The benzene molecule is the most stable. Ethyldiacetylene is 20% less stable than benzene and 30% less stable than the isomeric dimethyldiacetylene. However, the molecular-ion peak is the maximal peak in the spectrum of all four compounds.

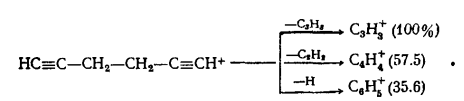
The ion-intensity distribution curves of all the C_6H_6 hydrocarbons investigated have two maxima, corresponding to the $C_6H_x^+$ and $C_4H_x^+$ ions[89]. The $C_6H_x^+$ group includes fragmentation ions from $(M-1)^+$ to $(M-5)^+$ in addition to molecular ions. The $(M-1)^+$ and $(M-4)^+$ ions are the most intense ions in the ethyldiacetylene spectrum. The $C_4H_x^+$ group includes ions formed from the parent ion by removal of two carbon atoms and different numbers of hydrogen atoms. Most of the ions of this group are capable of rearranging and are formed by the rupture of more than one C–C bond.

The removal on electron impact of one carbon atom with the formation of $C_5H_x^+$ ions is a process characteristic only of ethyldiacetylene. The peak of rearrangement ions of mass 64, corresponding in empirical formula to methyldiacetylene, shows the highest intensity in this group. The ability of the ethyldiacetylene molecular ion to dissociate with the formation of $C_5H_x^+$ ions appears to be related to the fact that this is the only hydrocarbon of those considered that can give fragments with rupture of a (less stable) bond in the β-position to the conjugated system.

Reduction of the energy of ionising electrons seriously affects the distribution of intensities only at energies lower than 30 eV. Near the ionisation threshold, differences in the spectra of ethyldiacetylene, divinylacetylene, and benzene are levelled out. It has been shown that the ionisation potentials of ethylacetylene, divinylacetylene, and benzene are quite similar.

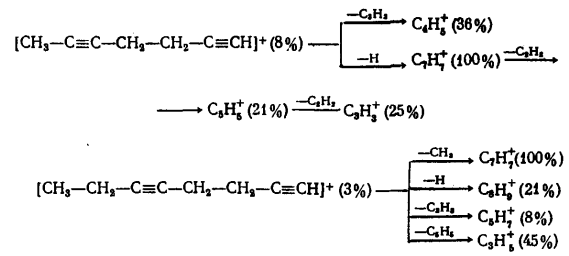
1. 1,5-Unconjugated Diynes

Because of the absence of conjugation, hexa-1,5-diyne, hepta-1,5-diyne, and octa-1,5-diyne are relatively unstable to electron impact[90]. The main decomposition route, the formation of fragmentation ions by cleavage of the molecular ion at the bond in the β-position to the acetylene grouping, may be represented by the following schemes:



In the mass spectra of methyl- and ethyl-dipropargyl, the maximum intensity is shown by peaks of $C_7H_7^+$ fragmentation ions. The molecular-ion peaks are low (8.2 and 2.6% of the maximum). The $C_7H_7^+$ ions appear to be produced by rupture of an outer β-bond, with elimination of hydrogen or a methyl group. These ions may have a cyclic "tropylium" structure. They decompose further according to the general scheme (with elimination of acetylene molecules). In this respect, the mass spectra of 1,5-diynes

are very similar to the spectra of the isomeric C_nH_{2n-6} hydrocarbons with conjugated multiple bonds.

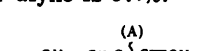


The decomposition of molecular ions of methyl- and ethyl-dipropargyl hydrocarbons at an inner β-bond occurs to only a slight extent, if at all. The spectrum of methyldipropargyl shows a peak corresponding to the $C_4H_5^+$ ion, which may in fact be produced in this way, but the presence of a peak of a metastable ion of mass 30.8 (0.2%) indicates that this ion is formed, at least partly, by the reaction $C_7H_7^+ \rightarrow C_4H_5^+ + C_2H_2$. The relative content of the analogous $C_5H_7^+$ ion in the ethyldipropargyl spectrum is small. The $C_5H_5^+$ ion in the ethyldipropargyl spectrum is formed mainly by the transition $C_8H_9^+ \rightarrow C_5H_5^+$ as is indicated by the presence of a metastable ion of mass 40.3. As a result of these reactions, the curves for the distribution of intensities show three maxima for hexa-1,5-diyne (corresponding to the ions $C_3H_x^+$, $C_4H_x^+$, and $C_6H_x^+$), two maxima for hepta-1,5-diyne ($C_4H_x^+$ and $C_7H_x^+$), and three maxima for octa-1,5-diyne ($C_3H_x^+$, $C_5H_x^+$, and $C_7H_x^+$). The low intensity of rearrangement ions in comparison with isomers containing conjugated bonds is a particular feature of the spectra of 1,5-diynes.

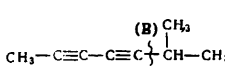
2. 2,4-Conjugated Diynes

The effect of conjugation on the behaviour of molecules under electron impact can be studied on the mass spectra of 2,4-diyne hydrocarbons[91] and of the alkenylvinylacetylenes[92]. It has been shown above that, in the spectra of hexa-2,4-diyne and in the spectra of the remaining isomers, the maximal intensity is exhibited by the peak of the molecular ion, which is inferior only to the benzene ion in its stability. With 6-methyl- and 6,6-dimethyl-hepta-3,4-diyne, decomposition of the molecular ion begins to play a much greater part; stability to electron impact decreases steadily from 30.9% for hexa-2,4-diyne to 5.9% for 6,6-dimethylhepta-2,4-diyne. The diversity of dissociative ionisation processes is reflected in the distribution of intensities. The curve of intensity distribution has two maxima, corresponding to the $C_4H_x^+$ and $C_6H_x^+$ ions. The maxima of the hydrocarbons C_8H_{10} and C_9H_{12} are displaced by one carbon atom.

The relatively low proportion of $C_3H_3^+$ ions is noteworthy and indicates that the probability of rupture of the central bond (A) in hexa-2,4-diyne is 3.7%:



In the spectra of hexa-2,4-diyne homologues, the $C_3H_3^+$ ion can be formed in a different way, namely, by rupture of the bond (B) and removal of hydrogen atoms from the propyl group.



This process results in some increase in the probability of the formation of the $C_3H_3^+$ ion; the peak intensity of ions of mass 39 becomes 7.9% of the full ion current; the proportion of $C_3H_3^+$ ions in the spectrum of 6,6-dimethylhepta-2,4-diyne relative to the full ion current is the same (7.4%). Removal of a methyl group, which is necessary for this process, meets with no difficulties, in so far as it is associated with rupture of a carbon–carbon bond in the β-position to the multiple bond.

It is very difficult to interpret the mechanism of formation of $C_4H_x^+$ ions, which are probably formed by removal of two methyl groups and migration of hydrogen atoms to a fragment with conjugated bonds. The ions $C_5H_x^+$, $C_7H_x^+$, $C_6H_x^+$, and $C_8H_x^+$ also appear to be formed by processes in which extensive isomerisation occurs. The first stage is probably effected by rupture of a bond in the β-position to the triple bond, and removal from the molecular ion of a methyl group derived from an isopropyl or t-butyl group, with the formation of $C_7H_x^+$ and $C_8H_x^+$ ions.

3. Alkenylvinylacetylenes

The mass spectra of the isomeric alkenylvinylacetylenes (C_7H_8), propenyl-, isopropenyl-, and allyl-vinylacetylene, show a similar distribution of intensities[92]. The maximal peak corresponds to the $C_7H_7^+$ ion; ions of mass 65 and 63 are also formed in large quantities. The probability, W_z, of decomposition of the parent ions depends on the structure of the alkenyl group (Fig. 8). Isopropenylvinylacetylene (W_M = 16.4%) is the most stable to electron impact. The intensity of the $C_7H_7^+$ ion peak is 18.3%, and the total proportion of fragmentation ions is 84.6%. The allylvinylacetylene molecular ion undergoes somewhat more extensive conversion (W_z = 81.2%); the proportion of $C_7H_7^+$ ions is 32.1%. Of the three isomers studied, propenylvinylacetylene undergoes the most extensive decomposition (W_z = 92.3%), but the quantity of ions of mass 91 and 65 is 1.9 and 2.4 times greater respectively than for isopropenylvinylacetylene.

Crotylvinylacetylene and its isomer, allylisopropenylacetylene, mainly dissociate in the same way as C_7H_8 hydrocarbons; the maximal intensity in their spectra is shown by the $C_7H_7^+$ ion peak; the stabilities of the parent ions are 9.8 and 7.7% respectively.

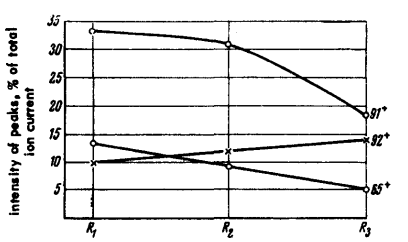
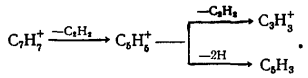


Fig. 8. Effect of structure of alkenyl group on probability of formation of molecular and fragmentation ions: R_1 = (CH_3–CH=CH–); R_2 = (CH_2=CH_2–CH_2–); R_3 = (–C(=CH_2)–CH_3).

Comparison of the mass spectra of dienyne hydrocarbons with the spectra of aromatic hydrocarbons, cycloheptadiene[84,87], and alkyl vinylacetylenes[81], not only indicates certain analogies in the distribution of ion intensities, but also suggests the existence of a general mechanism for the formation of separate typical ions. Evidently, in many instances in which the hydrocarbon molecule contains seven or more carbon atoms, the carbon skeleton rearranges to a seven-membered ring, and this excited ion acts as the main source of other fragmentation ions.

It may be assumed that when dienyne hydrocarbons dissociate the $C_7H_7^+$ ion formed acquires the structure of the tropylium ion, which may then undergo cleavage according to the following scheme:



Since all seven hydrocarbon atoms of the tropylium ion are equivalent, acetylene may be eliminated in several ways, which considerably increases the probability of this process. The above-mentioned scheme for the decomposition of the $C_7H_7^+$ ion formed by the dienyne hydrocarbons C_7H_8 and C_8H_{10} is confirmed by the presence in the spectra of these hydrocarbons of a metastable ion of mass 46.6 (intensity 0.5%).

The general scheme of dissociative ionisation becomes somewhat more complicated in higher members of the series (Fig. 9). At the first stage of decomposition, a methyl group is removed, and the most intense peak in the spectrum is formed ($C_8H_9^+$ ion); the position of the methyl group does not materially affect the peak intensity of these ions. Other fragmentation ions appear to be formed by removal of acetylene molecules, methylene groups, and hydrogen from the $C_8H_9^+$ ion.

Since fragmentation ions in the mass spectra of C_7–C_9-dienyne hydrocarbons are formed by a common mechanism, it may be that in the dissociation of $C_8H_9^+$ ions the carbon skeleton also rearranges to a seven-membered ring. These conclusions are in good agreement with the results of a study of the mass spectrum of tetrahydronaphthalene[93], in which the ions $C_8H_8^+$ and $C_7H_7^+$ are formed from the molecular ion $C_{10}H_{12}^+$ by elimination of C_2H_4 and C_3H_5 respectively. A cyclic structure can be ascribed to the ions $C_8H_8^+$ and $C_7H_7^+$ — that of cyclo-octatetraene to the first, and that of tropylium to the second.

The cyclic structure of ions in the gas phase, particularly of the tropylium ion, may explain the absence of material differences in the mass spectra of the isomers of dienyne hydrocarbons and the similarities of these spectra to the spectra of hydrocarbons of other groups, such as alkylbenzenes, cycloheptatriene, and styrene, and also to the spectra of compounds other than hydrocarbons.

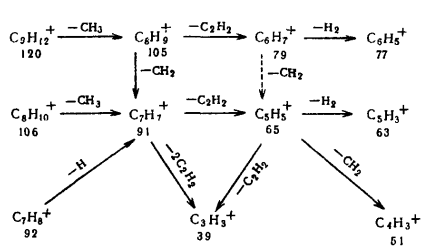


Fig. 9. Scheme of dissociative ionisation of dienyne hydrocarbons.

4. Alkylbenzenes

The most marked effects of conjugation on dissociative ionisation are shown by benzene and its homologues.

Benzene and its homologues are highly resistant to electron impact; the stability, which is 33% for benzene, decreases somewhat with increasing molecular weight, but it remains fairly high, averaging about 10% of the total ion current.

The alkylbenzenes dissociate mainly by rupture of the bond in the β-position to the benzene ring. The process includes the removal of a hydrogen atom from toluene, or from the alkyl group of other homologues, and the formation of a phenylalkyl ion. Sometimes, rupture of the β-bond is accompanied by migration of hydrogen with the formation of an alkylbenzene ion and an alkene.

Other things being equal, the mode of decomposition of the alkylbenzene molecule depends on the size and chain length of the alkyl groups attached to the benzene nucleus[84]. The main dissociation products of monoalkylbenzenes are ions formed by rupture of the side-chain at the β-bond. The size and chain length of the substituents at the α-carbon atom also affect the distribution of intensities.

Alkylbenzenes with the structure PhC(X)(Y)Z have been used in studies on the main modes of decomposition[84]. If X and Y = H, and Z is a group larger than the methyl group, rupture of the Y–C bond is accompanied by migration of hydrogen to the ion containing the ring. The probability of this migration, which is measured by the ratio of the heights of the ion peaks for masses 91 and 92, increases with increasing chain length. If X = H, and Y and Z are groups larger than the methyl group, appreciable peaks corresponding to the rupture of single bonds appear, and, for normal groups, the intensity of these peaks is directly proportional to the number of carbon atoms in the groups lost. If X and Y are methyl groups and Z is any alkyl group, significant peaks corresponding to ions of mass 91 are observed.

The probability of dissociation at an α-bond also varies with the substituent groups at the α-carbon atom. Branching at the α-carbon atom favours rupture at the α-bond.

Rylander and Meyerson[85], and also Hanuš[87], showed that the formation of the most intense ions in the mass spectra of alkylbenzenes is associated not only with migration of hydrogen, but also in many instances with rearrangement of the carbon skeleton. Detailed study of the mass spectra of deuterated toluenes shows the the probability of removing any of the hydrogen atoms from the molecule is the same. It may therefore be assumed that the carbon skeleton of the molecular ion rearranges, and all the carbon atoms become equivalent[94,95]. Various phenomena observed when alkylbenzenes interact with electrons, and not hitherto explained, become clear if it is assumed that in dissociative ionisation one of the most intense ions in the spectra of these compounds ($C_7H_7^+$) isomerises to the highly stable tropylium ion[96]. This hypothesis explains the stabilisation of the phenyl ion when the first methyl group is introduced into benzene by rearrangement of the benzenoid ion to the symmetrical, stable tropylium ion.

The introduction of a second methyl group does not change the fundamental structure of the ion and therefore has no effect on its stability. The existence of the tropylium ion also explains the identical distribution of intensities in the mass spectra of *o*-, *m*-, and *p*-dialkylbenzene isomers.

In the dissociation of polyalkylbenzenes, most of the ions are formed by rupture of a β-bond (with the exception of examples in which the side-chains consist of methyl or ethyl groups). As the number of side-chains increases, so does the number of bonds and therefore the number of possible characteristic peaks. Rupture at the β-bond in some chains, and at the α-bond in others, can lead to appreciable formation of peaks of ions of mass 91. Dialkylbenzenes with two groups larger than the methyl group behave differently. Dissociation occurs preferentially at the centre of the longest side chain with the greatest amount of branching at the α-carbon atom. If all the side-chains are short (for example, methyl groups), rupture at the α-bond predominates over β-rupture. The maximal peak for the polymethylbenzenes usually corresponds to $(M - 15)^+$ ions. With polyethylbenzenes, two competing processes that depend on structure are observed; these lead to the formation of about equal amounts of $(M - 15)^+$ and $(M - 29)^+$ ions.

The isomeric polyalkylbenzenes, which differ only in the position of the side-chains in the ring, generally have similar spectra. The intensity distribution of the ions obtained by electron bombardment does not permit the *ortho*-, *para*-, and *meta*-positions to be distinguished.

Notwithstanding some differences in the behaviour of the polyalkylbenzenes, their mass spectra have much in common, in particular these spectra show the preferential formation of ions of mass 77, 78, 91, 92, 105, 106, 119, 120, 133, 134, 147, 148, 161, and 162; on an average these ions make up 60% of the total ion current. The spectra of all polyalkylbenzenes show the presence of ions of mass 77, 78, and 79, and also of ions of mass 91, 92, 93, 105, 106, and 107, which are formed by rupture of the side chains at α- and β-bonds. The peaks of these ions are the most specific for establishing a relationship between structure and spectra. A clearly-defined system for the identification of 34 alkylbenzenes containing up to 24 carbon atoms in the side-chain has been worked out on the basis of mass spectra[84].

We shall not deal with polycyclic aromatic hydrocarbons. It should be noted, however, that as the number of condensed rings in the molecule increases the stability to electron impact increases, and W_M is a linear function of the ratio of the numbers of carbon and hydrogen atoms in compounds with different numbers of rings[97].

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Examination of the mass spectra of hydrocarbons of different homologous series has shown that, as the degree of unsaturation increases, large fragmentation ions tend to be stabilised, and this is reflected in the distribution of ion intensities (Fig. 1).[98] The distribution curve of alkanes and monoalkenes shows a single well-defined maximum, corresponding to $C_3H_x^+$ ions. A study by Coggeshall[99] of the mass spectra of alkane and alk-1-ene hydrocarbons showed that the proportion of ions containing the same number of carbon atoms (m) in relation to the full ion current has a maximum in the region where $m = 3-4$, the maximum of the alkene curve being displaced towards larger values of m.

One maximum, corresponding to $C_5H_x^+$ ions, also appears on the distribution curve of C_nH_{2n-2} ions. For enyne hydrocarbons (C_nH_{2n-4}), the second maximum is displaced in the direction of ions of greater mass ($C_6H_x^+$). $C_7H_x^+$ ions show a high intensity in the spectra of the alkenylvinylacetylene hydrocarbons (C_nH_{2n-6}). Fig. 10 illustrates this tendency towards reduced formation of ions of relatively low mass as the degree of unsaturation of the hydrocarbons increases.

This tendency is not confined to hydrocarbons; it is also shown by a number of cyclic fluoro-compounds[100].

The observed displacement of maxima on the distribution curves towards heavier ions appears to be related to the possibility of stabilisation of these ions as conjugated or cyclic structures, and it is no doubt also associated with processes in which rearrangements occur[98]. $C_3H_3^+$ ions play the main part in the formation of the first maximum, corresponding to $C_3H_x^+$ ions; in the formation of the second maximum in the spectrum of C_nH_{2n-2} hydrocarbons, corresponding to $C_5H_x^+$ ions, the main part is played by $C_5H_5^+$ and $C_5H_7^+$ ions and by C_5H_8. In dissociative ionisation of 3,4-dienes, the $C_5H_7^+$ ion may acquire the stable structure of the cyclopentyl ion, but in the case of 2,3-dienes stabilisation occurs by transfer of hydrogen to give the $C_5H_8^+$ ion. Curves showing the effectiveness of ionisation indicate that the processes that lead to the formation of $C_5H_7^+$ and $C_5H_8^+$ ions are quite general[74].

The main $C_6H_x^+$ ions in the mass spectra of C_nH_{2n-4} hydrocarbons are $C_6H_5^+$ and $C_6H_7^+$. These ions are also characteristic of the first members of homologous series of the general formula C_nH_{2n-6}.

Attempts have been made to obtain an idea of the structure of the $C_6H_x^+$ ion from an examination of the mass spectra of benzene and its open-chain isomers[89,90,101]. The appearance potentials of fragmentation ions and their enthalpies of formation indicate isomerisation of the excited molecular ion of benzene to a structure of the type:

$$(CH_2{=}CH{-}CH{=}CH{-}C{=}CH)^+.$$

The heat of isomerisation corresponds to the excited electronic state of the benzene ion (10.3 eV) observed by the photoionisation method. The molecular ion $C_6H_6^+$, which has a linear structure with a conjugated system of multiple bonds, dissociates in turn to form the fragmentation ions $C_6H_5^+$ and $C_6H_4^+$, which are also linear in their ground states. The high degree of unsaturation of the ions $C_6H_6^+$, $C_6H_5^+$, and $C_6H_4^+$ is responsible for the high probability of processes in which hydrogen migrates and $C_6H_7^+$ ions are formed; these

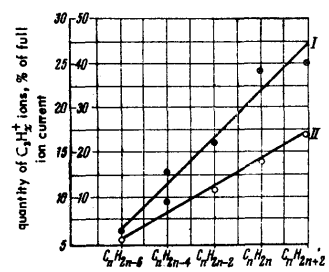

Fig. 10. Selectivity of dissociation of different types of hydrocarbons C_8 (*I*) and C_{10} (*II*).

ions are present in the spectra of vinylalkylacetylenes to the extent of 30–40% of the total ion current. Similar processes probably give rise to the formation of ions of mass 77, 78, and 79 in the mass spectra of some alkylbenzenes[102].

Dienynes and the isomeric alkylbenzenes show maxima on the distribution curves corresponding to $C_3H_x^+$ and $C_5H_x^+$ ions that are characteristic of highly unsaturated compounds; moreover, the isomeric C_7H_8 and C_8H_{10} hydrocarbons, such as toluene, ethylbenzene, and xylene, have a third maximum for $C_7H_x^+$ ions. For C_9H_{12} hydrocarbons, this maximum is displaced in the direction of the heavier $C_8H_x^+$ ions.

To obtain a more precise idea of the structure of rearranged ions produced in the dissociative ionisation of highly unsaturated compounds, the authors determined the potentials at which $C_3H_3^+$, $C_5H_5^+$, and $C_7H_7^+$ ions were produced from alkyl- and alkenyl-vinylacetylenes. Using these potentials and the known heats of formation of the molecules, they were able to calculate the heats of formation of the ions, decide between different possible ionic structures, and establish the mechanism by which these are formed. The heats of formation of $C_3H_3^+$ ions obtained from different hydrocarbons are close to one another (292–294 kcal mole^{-1}); it is possible that $C_3H_3^+$ ions acquire a cyclic structure, which can be assigned to them in the same way as to quasiaromatic systems[95]. Within the limits of experimental error, the heats of formation obtained for $C_7H_7^+$ ions coincide with the heat of formation of the tropylium ion (238–240 kcal mole^{-1})[86], which undoubtedly indicates that these ions have a cyclic structure.

Study of the mass spectra of toluene and its isomers, cycloheptatriene, spiro[2,4]hepta-1,3-diene, bicyclo[2,2,1]-hepta-2,5-diene[103], and 7d-cycloheptatriene[104] has shown that always the intermediate excited particle produced by dissociative ionisation is the tropylium ion, $C_7H_7^+$, from which other fragmentation ions are formed:

$$C_7H_8^+ \rightarrow C_7H_7^+ \rightarrow C_5H_5^+ \rightarrow C_3H_3^+ \text{ and } C_7H_8^+ \rightarrow C_5H_6^+.$$

The cyclic structure of ions in the gas phase, in particular the structure of the tropylium ion and its homologues, explains the absence of substantial differences between the mass spectra of isomers of dienyne hydrocarbons and also the analogies of these spectra to the spectra of alkylbenzenes, cycloheptatriene, and some compounds other than hydrocarbons.

Examination of the mass spectra of hydrocarbons containing different numbers of multiple bonds in the molecule shows that the quantity of ions produced by rearrangement increases with the number of multiple bonds in the molecule[98,105]. In other words, rearrangement ions in the mass spectra of hydrocarbons are characteristic of the degree of unsaturation and may be used for the qualitative and quantitative analysis of hydrocarbons.

A characterististic such as complete ionisation is directly related to the structure of hydrocarbons and their degree of unsaturation, and it can be used in the quantitative evaluation of interactions of ionising electrons with molecules. The available experimental results clearly prove that any attempt to express the relative ionisation cross-section of molecules as the sum of the cross-sections of the atoms would not reflect the true situation.

It has been shown that different isomers of many types of highly branched hydrocarbons containing multiple bonds differ in their complete ionisation potentials, which is probably due to wide differences in the electron-density distribution of the molecules. Thus, Table 1 gives the values for complete ionisation (relative to benzene) of isomeric diene hydrocarbons.

TABLE 1.

C_9H_{14}	Complete ionisation	$C_{10}H_{18}$	Complete ionisation
$(CH_3)_3C'-CH=CH-CH=CH_2$	1.18	$H_3C-H_2C-HC=C=CH-CH_2-CH_2-CH_2-CH_3$	1.81
$CH_3-CH=CH-CH_2-CH_2-CH_3$	1.40	$H_3C-CH_2-HC=C=CH-CH_3-C(CH_3)_2$	1.81
CH_2-CH_3			
$H_3C-HC=C=CH-CH_2-CH_2-CH_2-CH_3$	1.87	$CH_3(C_2H_5)_2C-CH=CH-CH=CH_2$	2.19

Complete ionisation is certainly not always directly related to molecular weight. In the alkylbenzene homologous series, complete ionisation is a linear function of the number of carbon atoms in the molecule, but the converse is true of 1,5-diynes, as is shown by the figures in Table 2.

At present there is no explanation of this effect, and the problem remains to be solved.

The establishment of empirical relationships between the structure of the molecule and its mass spectrum leads to the elucidation of the general principles that govern dissociative ionisation. Although the apparatus necessary for the quantitative calculation of mass spectra of individual compounds is not available, quantitative characteristics common to types of compounds can be calculated. In this connection, the use of curves showing the distribution of intensities against the number of carbon atoms in ions has proved very fruitful. Since the position of the maxima on the curves is determined by the value of z in the formula C_nH_{2n+z}, it is possible to establish the composition of a homologous series of ions specific to the hydrocarbon groups whose spectra are unknown[106]. On the other hand, the curves reflect special features in the molecular structure of isomers; this has been used as a basis for the determination of cyclopentane and cyclohexane hydrocarbons in complex mixtures, and for the identification of types of monoalkenes[61,63].

Mathematical treatment of the relationship between the characteristic intensity and the degree of unsaturation of different types of hydrocarbons has permitted the calculation of the corresponding mass-spectrometric coefficients for naphthene hydrocarbons with different numbers of condensed rings in the molecule. As a result, the lack of experimental calibration coefficients has been no hindrance to the development of methods of determining paraffins and naphthenes present in high-boiling petroleum fractions[107,108].

TABLE 2.

Number of carbon atoms in molecule	Complete ionisation	
	alkylbenzenes	1,5-diyne hydrocarbons
6	1	1
7	1.4	0.92
8	1.8	0.78

Correlations in the mass spectra of hydrocarbons have also been used in a new method of analysis, chromato--mass-spectrometry, developed by Tal'roze and co-workers[109-115].

These workers studied the problem of the minimum amount of mass-spectrometric information necessary for the unambiguous identification of individual compounds. It was shown that any individual compound reaching the mass spectrometer from the chromatograph can be identified with a high degree of probability, provided that two types of ratios of mass-spectrometric peaks are known in the 39-45 range of mass numbers. This enabled a mass spectrometer of low dispersion and resolving power to be used. The above authors have developed methods for the analysis of hydrocarbons and their derivatives by chromato-mass--spectrometry.

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RUSSIAN CHEMICAL REVIEWS
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SEMEN ISAAKOVICH VOL'FKOVICH

Dear Semen Isaakovich,

The Editorial Board of the Journal "Uspekhi Khimii" send you their heartfelt greetings on the occasion of your jubilee. As a member of the Editorial Board of this journal from the day of its foundation, you have rendered an enormous service to the journal and its readers. Your work in the field of chemistry and chemical engineering and, in particular, in the development of the manufacture of mineral fertilisers, is of great importance for the national economy of our country. We believe that your energy and your capacity for work will ensure that the fields which you will develop in the future will enrich both science and industry.

Your work on the training of chemists has gained general respect.

We wish you good health, many happy days, and even greater creative successes.

U.D.C. 631.8:631.816

STUDIES IN THE CHEMISTRY AND TECHNOLOGY OF MINERAL FERTILISERS IN THE USSR

A. A. Ionass, L. V. Vladimirov, and S. Ya. Shpunt

The progress in the chemistry and technology of the products of the basic chemical industry has been stimulated in recent years in all highly developed countries by the rapid growth of the application of chemistry to agriculture and the continuous increase of the requirements of many other branches of the national economy. The considerable increase in the manufacture and application of mineral fertilisers (by a factor of five in fifty years) has led to qualitative changes in the technological methods for their preparation, has greatly extended the range of fertilisers available and the industrial raw materials pool, and has led to great intensification of theoretical and practical research. A considerable contribution to the development

of the chemistry and technology of mineral fertilisers, acids, and salts, has been made by the Fertilisers, Insecticides, and Fungicides Institute, founded soon after the October Revolution on the initiative of Ya. V. Samoilov, E. V. Britske, and D. N. Pryanishnikov. In this Institute fundamental research has been carried out, which ensured the creation in the USSR of a large-scale mineral fertilisers industry and its raw materials base and had led to the determination of the requirement for effectiveness and the conditions of application of fertilisers in agriculture. Extensive and creative studies have been made by the Institute in the chemistry and technology of sulphuric, nitric, phosphoric, and hydrofluoric acids, insecticides, fungicides, and herbicides.

Semen Isaakovich Vol'fkovich, who celebrated his 70th birthday on the 23rd October 1966, has been one of the principal scientific leaders of this large collective of chemists, engineers, and other specialists over a period of more than 40 years (he set up his own school). Extensive studies, which led to the development of new ways of manufacturing phosphorus fertilisers and a whole series of advanced processes for the preparation of potassium, nitrogen, boron, and complex fertilisers, have been made by Vol'fkovich and his coworkers and students. They have done much work on the chemistry and technology of the compounds of fluorine, sulphur, selenium, and rare earths, and certain organic compounds. The work of Vol'fkovich and coworkers on the chemistry and technology of phosphorus and its compounds has been of the greatest importance. He began with the study of the production of phosphorus by the reduction, in an electric furnace, of phosphates naturally occurring in the USSR, which served as the starting point of many years of further investigations by planning and production engineers, and then passed on to the study and development of other thermal reactions involving the processing of phosphates by their interaction with alkali metal salts and treatment with water vapour. An extensive and detailed cycle of investigations was devoted to the development of the processing of phosphates by their interaction with sulphuric, nitric, and hydrochloric acids.

The physicochemical studies of equilibrium systems and the kinetics of the decomposition of natural phosphates, particularly closely related to the methods of manufacture of fertilisers from the raw materials available in the USSR and the complex utilisation of the latter, have proved very important in the development and progress of the processes described above.

A large proportion of the phosphate deposits prospected up to 1927 in the USSR were of lower quality than the North African, American, and island phosphorites. During the first years of the industrialisation of our national economy, Soviet superphosphate factories encountered many difficulties in the processing of inferior local phosphorites, while in 1930 further difficulties were encountered in the transition to a new type of raw material (new throughout the world and not just in the USSR) — the Khibinsk apatite concentrate. The Khibinsk deposit of apatites and nephelin ores huge and unique as regards composition and properties, differs significantly from the African and American phosphates used up to that time. This difference required a more extensive study of the structure of apatite and the reactions involved in its processing.

Together with Berlin[1-10] and other coworkers, Vol'fkovich studied the kinetics of the decomposition of fluoroapatite and other minerals associated with it, which led to the decision to enrich the ore, and optimum conditions were established for the conversion of the apatite concentrate into superphosphate. This process involves two main stages:

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 2.5H_2O = 3H_3PO_4 + 5(CaSO_4 \cdot 0.5H_2O) + HF,$$

$$Ca_5F(PO_4)_3 + 7H_3PO_4 + 5H_2O = 5[Ca(H_2PO_4)_2] \cdot H_2O + HF.$$

The first stage takes place in the reactor and is completed in the presence of a large excess of sulphuric acid over the stoichiometric amount required for the preparation of $Ca(H_2PO_4)_2$, the process being localised in the surface layer of the initial phosphate particles. In this stage calcium sulphate is precipitated as the hemihydrate. The second stage begins at a temperature in excess of 110°C and under these conditions the hemihydrate is converted into the anhydrous anhydrite. Despite the negative conclusions of a number of foreign specialists, studies in the laboratory and in factories under operating conditions established not only the possibility but the advantage of the processing of the apatite concentrates which made it possible to apply the technological scheme for the manufacture of superphosphate thus developed in all Soviet and certain foreign undertakings.

The development of the mineral fertilisers industry in the USSR made urgent a more profound study of the raw material, and the development of new technological methods for its processing. As early as 1927–1928 the decision was taken at the Fertilisers, Insecticides, and Fungicides Institute to obtain concentrated fertilisers and to develop a new method of the acid processing of phosphates. Vol'fkovich, Kamzolkin, and others[11-13] studied the complex processing of phosphates designed to prepare concentrated fertilisers, ammonium phosphates, and double and enriched superphosphate, with simultaneous synthesis of nitrogen fertilisers. The method consisted essentially in the decomposition of phosphate by mixtures of sulphuric acid and ammonium sulphate which led to economy in the use of sulphuric acid and higher purity of phosphoric acid obtained from interior phosphorites contaminated with iron and aluminium oxides. The "phosphogypsum" thus obtained is decomposed with ammonia and carbonic acid or ammonium carbonate, yielding ammonium sulphate and calcium carbonate. The ammonium sulphate is recovered in the process involving extraction with phosphoric acid, which is neutralised by ammonia or is used to decompose natural phosphate. The extraction of phosphoric acid and its neutralisation by ammonia have been studied in detail at the Fertilisers, Insecticides, and Fungicides Institute, and have been used in industry: the preparation of ammonium sulphate from phosphogypsum was tested under pilot plant conditions.

The studies carried out by Belopol'skii, Taperova, Shpunt, and others[14-16] on the kinetics of the decomposition and the solubility of the hydrates of calcium sulphate and its phase transformations in the system $CaO-P_2O_5-SO_3-H_2O$ served as a basis for the manufacture of phosphoric acid and superphosphate. The studies showed that within this system $CaSO_4.2H_2O$, $CaSO_4.0.5H_2O$, and $CaSO_4$ are formed. $CaSO_4.2H_2O$ is the principal component of phosphogypsum, obtained in the manufacture of phosphoric acid; it is the metastable component of the system and since the induction period in its conversion is very long, it is stable within the limits of the manufacturing cycle.

The studies of the solubilities of calcium sulphate hydrates in aqueous phosphoric acid were made at 25° and 80°C. It was shown that anhydrite is the least soluble and hence the only stable solid phase at 80°C.

The relative stabilities of gypsum and the hemihydrate vary with the concentration of phosphoric acid. At concentrations less than 33% P_2O_5 the dihydrate is less soluble and is therefore more stable than the hemihydrate. The opposite behaviour is found at concentrations in excess of 33% P_2O_5. The solubility curves for gypsum and the hemihydrate intersect at a P_2O_5 concentration of 33% at 80°C. These conditions correspond to the reaction

$$CaSO_4 \cdot 2H_2O \rightleftarrows CaSO_4 \cdot 0.5\,H_2O.$$

The system $CaSO_4$–H_3PO_4–H_2O was studied at 25°C and phosphoric acid concentrations between 0 and 63% P_2O_5. It was shown that, at all phosphoric acid concentrations, the first solid phase precipitated at 25°C and 80°C is the hemihydrate, which is rapidly hydrated to gypsum at low concentrations (9–20% P_2O_5). The study of the solubility of calcium sulphate hydrates at 25°C showed that there are two intersections of the solubility curves. The first intersection is at 33.7% P_2O_5, gypsum being the solid phase; above 33.25% anhydrite is the stable phase. At a concentration of 49% P_2O_5 the solubility curve for gypsum intersects the solubility curve for the hemihydrate. Under these equilibrium conditions gypsum and the hemihydrate are metastable, being converted into anhydrite. Thus the reactions of calcium sulphate in phosphoric acid at 25°C are as follows:

Below 33.75% P_2O_5 in solution	Between 33.75 and 49.0% P_2O_5 in solution	Above 49.0% P_2O_5 in solution
$CaSO_4 \cdot {}^1/_2 H_2O$	$CaSO_4 \cdot {}^1/_2 H_2O$	$CaSO_4 \cdot 2H_2O$
↓	↓	↓
$CaSO_4$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot {}^1/_2 H_2O$
↓	↓	↓
$CaSO_4 \cdot 2H_2O$	$CaSO_4$	$CaSO_4$

The studies showed that at 80°C the only stable solid phase is anhydrite. At 25°C the stable phases are anhydrite above 33.75% P_2O_5 and gypsum below this concentration. The hemihydrate is metastable at all phosphoric acid concentrations. In solutions with concentrations between 33.75% and 49% P_2O_5 gypsum is more stable than the hemihydrate, while above 49% P_2O_5 the opposite relation obtains. In these studies the kinetics of the transformations of various calcium sulphate hydrates were also investigated, which made it possible to construct a polythermal induction period isochrone diagram [to determine the temperature variation of the compositions corresponding to constant induction periods? (Ed. of Translation)], on the basis of which it was suggested that concentrated phosphoric acid be prepared with elimination of calcium sulphate in the form of anhydrite.

The most important chemical-technological factor in the manufacture of phosphoric acid is the formation and elimination of calcium sulphate. The form, particle size, and homogeneity of the calcium sulphate formed and the presence of impurities in the acid have a decisive influence on the separation of the sulphate from phosphoric acid, which is achieved by means of filters of various design and decanting devices; impurities also affect the conditions and degree of washing of the precipitate and hence the extraction coefficient of the phosphoric acid.

Until physicochemical analysis led to the elucidation of the details of the crystallisation of various forms and modifications of calcium sulphate in the manufacture of phosphoric acid by its extraction from phosphorites with sulphuric acid, it was difficult to ensure the formation, in the manufacturing process, of large phosphogypsum crystals which could be easily filtered. On the basis of physicochemical studies, Vol'fkovich, Voskresenskii, and others [17-20] carried out technological investigations of the crystallisation of phosphogypsum, in which they determined the conditions for the formation of highly crystalline, and hence easy to filter, calcium sulphate deposits, which enabled a highly effective technological scheme to be developed. On the basis of these data, factories have been planned and constructed in which phosphoric acid is manufactured to this day by the sulphuric acid decomposition method (Voskresensk, Vinnitsa, Volkhovsk, Krasnoural'sk, and other factories).

In view of the intense development of the industrial synthesis of ammonia and nitric acid, Vol'fkovich undertook as early as the 1930's the development of processes for nitric acid decomposition of phosphates. The advantage of these processes consists in the manifold utilisation of the reacting phosphate and nitric acid, the energy of the reaction being used at the same time for the decomposition of the phosphate. Whereas in the manufacture of phosphoric acid and concentrated fertilisers by sulphuric acid and hydrochloric acid decomposition, phosphogypsum and calcium chloride are formed as the respective waste products, which leads to considerable industrial difficulties, in the processing of phosphates by nitric acid there is no waste. Vol'fkovich, Loginova, and Belopol'skii [21-26] elucidated the physicochemical and chemical-technological conditions for the processing of natural phosphates with nitric acid, with manifold utilisation of the raw material (phosphorus, fluorine, and rare earths).

Over a period of several years, Vol'fkovich and his coworkers investigated the chemistry and various modifications of the process using different types of raw material native to the USSR, which led them to propose original technological schemes. These schemes are based on the decomposition of fluoroapatite, the main component of natural phosphates:

$$Ca_5F(PO_4)_3 + 10HNO_3 = 3H_3PO_4 + 5Ca(NO_3)_2 + HF. \quad (1)$$

In the processing of natural phosphates the oxides of iron, aluminium, potassium, and sodium and silicic acid pass into solution in addition to nitric, phosphoric, and hydrofluoric acids; in the processing of the Khibinsk apatite lanthanides also dissolve. Vol'fkovich suggested that the solution prepared by reaction (1) be converted into concentrated and complex fertilisers [25]. One of the modifications of the process proposed and developed together with Loginova consisted in the cooling of the solution (extract) as a result of which calcium nitrate crystallised out and could be separated, which ensured that on further neutralisation with ammonia solution the phosphates were obtained in partially or completely soluble form (depending on the temperature to which the solution was cooled). Calcium nitrate may be used as such or converted by treatment with ammonia and carbonic acid into ammonium nitrate or decomposed by heating into calcium oxide and nitrogen oxides, which are returned to the manufacturing cycle. The isolation of calcium sulphate from solution with the aid of ammonium sulphate was also investigated. On neutralisation with ammonia solution, ammonium phosphate or its mixture with dicalcium phosphate are formed by the reactions

$$H_3PO_4 + NH_3 = NH_4H_2PO_4, \quad (2)$$

or

$$3H_3PO_4 + 1.5\,Ca(NO_3)_2 + 4.5\,NH_3 = 1.5\,NH_4H_2PO_4 + 1.5\,CaHPO_4 + 3NH_4NO_3. \quad (3)$$

Following the addition of ammonium sulphate to the solution and neutralisation with ammonia, the overall reaction is

$$H_3PO_4+Ca(NO_3)_2+(NH_4)_2SO_4+NH_3+2H_2O=CaSO_4\cdot 2H_2O+NH_4H_2PO_4+2NH_4NO_3. \quad (4)$$

Calcium sulphate (gypsum) can be separated and then treated with carbonic acid and ammonia to yield ammonium sulphate which is returned to the process [reaction (4)].

On addition of potassium chloride or sulphate to the reaction mixture, a ternary fertiliser (Nitrophoskas), containing 52% of nutrient materials (N, P_2O_5, and K_2O), is obtained. In their study of the nitric acid decomposition of phosphates, much attention was given to the investigation of the system $CaO-P_2O_5-N_2O_5-H_2O$ [26] at 25° and 50°C. Table 1 presents data characterising the compositions of the liquid and solid phases at the nodal points of the isotherms[26]. The results obtained permitted a technological analysis of the nitric acid decomposition of phosphates, the determination of the theoretical proportions of the reactants, and the calculation of the limiting yields and the concentrations of the intermediate and final products formed in the process.

The method of nitric acid decomposition of phosphates proposed by Vol'fkovich eliminates the formation of waste in the manufacturing process by including stages in which stepwise neutralisation of the nitric acid extract is carried out by sodium, calcium, or ammonium salts, fluoride and rare earths being precipitated. The latter cannot be recovered in the sulphuric acid processing of phosphates.

Various methods of nitric acid processing of phosphates developed in the laboratories of the Fertilisers, Insecticides, and Fungicides Institute have been applied on the industrial scale in the experimental workshop of the Dneprodzerzhinsk nitrogen mineral fertilisers factory. Margolis, Dubovitskii, Glazova, and others participated in these studies[27,28].

TABLE 1.

Nodal points of the isotherms.

Designation of point (see Ref. 26)	Solution: wt.% CaO	wt.% P_2O_5	wt.% N_2O_5	moles per 1000 moles of H_2O: CaO	moles per 1000 moles of H_2O: P_2O_5	moles per 1000 moles of H_2O: N_2O_5	Solid phase
				25°C isotherm			
A	5.81	24.20	—	26.7	43.8	—	$Ca(H_2PO_4)_2\cdot H_2O + CaHPO_4$
N	19.73	1.18	37.26	151.7	3.6	148.5	$Ca(H_2PO_4)_2\cdot H_2O + CaHPO_4 + Ca(NO_3)_2\cdot 4H_2O$
M	19.79	traces	37.74	149.8	traces	149.8	$CaHPO_4 + Ca(NO_3)_2\cdot 4H_2O + Ca(NO_3)_2\cdot H_2O$
P	14.24	18.21	30.36	122.9	62.0	136.0	$Ca(H_2PO_4)_2\cdot H_2O + Ca(NO_3)_2\cdot 4H_2O + Ca(NO_3)_2\cdot 3H_2O$
B	11.03	—	51.89	95.4	—	233.1	$Ca(NO_3)_2\cdot 4H_2O + Ca(NO_3)_2\cdot 3H_2O$
C	9.54	—	56.28	89.5	—	274.3	$Ca(NO_3)_2\cdot 3H_2O + Ca(NO_3)_2\cdot 2H_2O$
D	2.79	—	62.84	26.1	—	304.6	$Ca(NO_3)_2\cdot 2H_2O + Ca(NO_3)_2$
				50°C isotherm			
A	5.88	28.85	—	28.9	56.0	—	$Ca(H_2PO_4)_2\cdot H_2O + CaHPO_4$
N	23.41	4.80	45.81	289.9	23.4	292.3	$Ca(H_2PO_4)_2\cdot H_2O + CaHPO_4 + Ca(NO_3)_2\cdot 2H_2O$
M	26.63	0.1	51.27	389.0	0.6	389.0	$CaHPO_4 + Ca(NO_3)_2\cdot 2H_2O + Ca_3(PO_4)_2\cdot H_2O$
P	20.79	11.12	43.28	269.3	56.4	290.6	$Ca(H_2PO_4)_2\cdot H_2O + Ca(NO_3)_2\cdot 2H_2O + Ca(NO_3)_2$
D	25.95	—	51.23	265.2	—	374.3	$Ca(NO_3)_2\cdot 2H_2O + Ca(NO)_2$

In the concentration range investigated the isotherms are characterised by the saturation fields of the following stable phosphates and nitrates:

	25°	50°
Phosphates	$CaHPO_4$ $Ca(H_2PO_4)_2\cdot H_2O$	$CaHPO_4$ $Ca(H_2PO_4)_2\cdot H_2O$
Nitrates	$Ca(NO_3)_2\cdot 4H_2O$ $Ca(NO_3)_2\cdot 3H_2O$ $Ca(NO_3)_2\cdot 2H_2O$	$Ca(NO_3)_2\cdot 2H_2O$ $Ca(NO_3)_2$

At the present time there are in the USSR two factories in which modified methods of nitric acid processing of phosphates are used, and two further factories are planned. Apart from the advantages of the use of nitric acid mentioned above, owing to the absence of waste and the twofold utilisation of the acid, for the decomposition of phosphates and as a component of the fertiliser, these manufacturing schemes can be employed in the processing of inferior iron-containing phosphorites.

The studies carried out under the direction of Vol'fkovich and Belopol'skii by the scientific team at the Fertilisers, Insecticides, and Fungicides Institute on the decomposition of natural sodium sulphate with ammonia and carbonic acid with production of sodium carbonate and ammonia sulphate are of theoretical and technical interest. This process is of particular interest in the USSR where there are large deposits of natural sulphate (Kara-Bogaz-Gol, the Aral sea, and others). The manufacture of sodium carbonate and ammonium sulphate from mirabilite consists in the double decomposition of sodium sulphate and ammonium bicarbonate:

$$Na_2SO_4+2NH_4HCO_3 \rightleftarrows (NH_4)_2SO_4+2NaHCO_3.$$

The 15°, 7°, 0°, -5°, -5.9°, -10°, and -17°C isotherms for the system $Na_2SO_4-NH_4HCO_3-H_2O$ were investigated[29-31] in order to set up a rational physicochemical basis for the development of a method of converting sodium sulphate into sodium carbonate and ammonium sulphate. The diagrams obtained in the study of the appropriate systems were used for practical calculations. Graphical calculation revealed the possibility of separating sodium and ammonium sulphates by freezing out. Combination of freezing and evaporation allows, in theory, the separation to be taken to completion, 100% utilisation of the initial sodium sulphate being thereby achieved (up to 95–97% in practice).

The physicochemical study of the carbonisation of aqueous ammonia solutions of sodium sulphate by Bolopol'skii and Urusov[32] permitted the calculation, on the basis of the equilibrium diagrams, of the optimum proportions of the reactants, the latter being confirmed by direct experiments on the carbonisation of aqueous ammonia solutions of sodium sulphate. Extensive experimental data yielded comparative coefficients characterising the course of the carbonisation in various zones of the carbonisation column and allowed an approach to the determination of the conditions which should be taken into account in the design of the usual Solvay columns to ensure the successful carbonisation of ammonia–sulphate solutions in the latter. To optimise the conditions of this process, Belopol'skii and Shpunt[33] investigated the partial pressure of ammonia, carbon dioxide, and water over ammonia–sulphate and ammonia–chloride solutions.

Semi-industrial and industrial experiments on the carbonisation of ammonia–sulphate solutions using appropriate apparatus[34] demonstrated the usefulness of the sodium carbonate column in the carbonisation of such solutions and yielded data required for the design and exploitation of apparatus for carbonisation, filtration, and calcination in the ammonia–sodium carbonate manufacture based on sodium sulphate.

Comparative technical and economic calculations indicate high economic efficiency of the process, which is a consequence of the manifold utilisation of the raw material and the absence of waste in the manufacturing process. The latter can be introduced for the processing of sodium sulphate (mirabilite from the Kara-Bogaz deposit and others).

To avoid the loss of sulphuric acid and the consumption of large amounts of electrical energy in the processing of phosphates, Vol'fkovich, Postnikov, Illarionov, Ionass, and Remen[35-38] investigated and developed a new hydrothermal process for the conversion of natural phosphates into fertilisers and fodder for animal husbandry. The process yields a highly concentrated mineral fodder additive containing up to 90% of useful substances, including about 40% P_2O_5 and 50% CaO, essential for the nutrition of animals. To obtain information about the reactions occurring in the hydrothermal processing of phosphates, it was necessary to investigate the systems $CaO-P_2O_5$ and $CaO-SiO_2-P_2O_5$. These systems have been the subjects of numerous investigations by Bredig et al.[39], Trömmel[40], and Barrete and McCoughey[41], who discovered the principal compounds formed under given conditions and established the regions of their existence. However, in these studies the system $CaO-P_2O_5-SiO_2$ was not investigated adequately in the range of low silica concentrations, and this region is of great importance for the hydrothermal processing of natural phosphates developed by Vol'fkovich and coworkers. Evseeva, Luzhnaya, and others[42] investigated the system at low concentrations of SiO_2 and showed that under these conditions the principal phase is $Ca_3P_2O_8$, which has a very small region of stability.

Until recently the mechanism of the hydrothermal process of natural phosphates remained obscure. The solution of this problem is not only of theoretical but also of practical importance for the industrial application of the process. In order to establish its mechanism[43], measurements were made of the heats of formation of hydroxoapatite and fluoroapatite and also the heat of decomposition of the Khibinsk apatite concentrate. The heat of formation of fluoroapatite is 3269 kcal mole^{-1} and that of hydroxoapatite 3211.9 kcal mole^{-1}. The heat of replacement of fluorine by a hydroxy-group in the reaction between fluoroapatite and water has been calculated from these quantities as 44.24 kcal.

On the basis of their own and literature data[44], these authors calculated the enthalpy differences and the entropies for hydroxoapatite (HA), fluoroapatite (FA), and water vapour in the temperature range 1000–1800°K, and also the thermodynamic functions and equilibrium constants for the reaction

$$Ca_{10}F_2(PO_4)_6+2H_2O \rightleftarrows Ca_{10}(OH)_2(PO_4)_6+2HF.$$

These quantities are listed in Tables 2 and 3.

TABLE 2. Enthalpy differences and entropies for hydroxoapatite fluoroapatite, and water vapour.

T, °K	$(H_T^\circ - H_{298.16}^\circ)$			S_T°		
	HA	FA	H_2O	HA	FA	H_2O
1000	166 130	159 710	6215	464.4	454.1	55.598
1300	247 890	237 310	9310	535.8	521.4	58.299
1600	332 795	315 000	12 636	593.0	575.1	60.640
1750	376 765	357 584	14 383	620.5	602.1	60.650
1800	391 628	371 374	14 994	628.8	605.9	61.650

TABLE 3. Thermodynamic functions and equilibrium constants for the reaction*.

$10^4/T$	$T_1^\circ K$	ΔH	ΔS	$\log K_e$	$\log K_e^1$	K_e^1
1	1000	48.166	43.430	−9.4929	−4.7465	0.0000179
0.76863	1300	50.591	40.084	−6.7396	−3.3698	0.000427
0.62500	1600	55.734	37.084	−5.1834	−2.5918	0.00250
0.57143	1750	56.163	34.876	−4.3561	−2.1780	0.00664
0.55560	1800	56.602	34.129	−4.1444	−2.0722	0.00847

* $K_e^1 = \sqrt{K_e} = P_{HF}/P_{H_2O}$.

For 1000° and 1300°K, literature data for higher temperatures were used, the enthalpy difference for fluoroapatite being calculated from the equation

$$(H_T - H_{298.16}) = 226.04\,T + 14.44 \times 10^{-3}T^2 + 48.82 \times 10^5 T^{-1} - 85\,050,$$

and for hydroxoapatite from the equation

$$H_T - H_{298.16} = 228.52\,T + 19.81 \times 10^{-3}T^2 + 50.00 \times 10^5 T^{-1} - 86\,670.$$

The enthalpy differences for water at 1000°, 1300°, and 1750°K were taken from Waggaman[45], while the values at 1600° and 1800°K were calculated from the equation

$$H_T - H_{298.16} = \int_{298.16}^{T} C_p dT.$$

The equilibrium constants K_e and K_e^1 confirm that the partial pressures of hydrogen fluoride in equilibrium with water vapour are very low. Thus, if it is assumed that, on isomorphous replacement of a fluoride ion by a hydroxide ion a new phase is formed, the reaction must be localised in the high-temperature zone (near the flame in the rotating furnace). If the process took place according to the mechanism indicated, involving the conversion of the fluoroapatite phase into the hydroxoapatite phase, then at 1375°C there would be no loss of fluorine. However, laboratory and then factory experiments showed that at this temperature fluorine is evolved, albeit slowly, and therefore there is a possibility of the formation of a phase of variable composition — fluorohydroxoapatite. Direct determination of the heat of decomposition confirms this hypothesis. Thus experiments show that the mechanism of the process can be represented by the following equations:

$$(1)\ Ca_{10}F_2(PO_4)_6+H_2O=Ca_{10}F(OH)(PO_4)_6+HF,$$

$$(2)\ Ca_{10}F(OH)(PO_4)_6+H_2O=Ca_{10}(OH)_2(PO_4)_6+HF,$$

$$(3)\ Ca_{10}(OH)_2(PO_4)_6=2Ca_3(PO_4)_2+Ca_4P_2O_9+H_2O.$$

Since the apatite concentrate contains only a small amount of silica, up to 2% of sand is added to it; in the presence of silica the reaction takes place as follows:

$$2\,Ca_5OH(PO_4)_3+\frac{1}{3}SiO_2=3Ca_3(PO_4)_3+\frac{1}{2}Ca_2SiO_4+H_2O.$$

In a general form the hydrothermal decomposition of apatite may be represented by the reaction

$$n\,Ca_{10}F_2(PO_4)_6+m\,SiO_2+H_2O=10\,nCaO\cdot 3nP_2O_5\cdot mSiO_2+2HF.$$

This process was investigated, under Vol'fkovich's direction, by Ionass, Remen, and others using the apatite concentrate and phosphorites from other deposits (Kara-Tau, Egor'evskoe deposit, Volgo-Vyatskoe deposit, and others[46]). Above it was shown that, by virtue of its low fluorine content and the absence of harmful impurities (lead and arsenic), the product obtained by this method, defluorinated phosphate, may be used not only as a fertiliser but also as a mineral calcium–phosphorus food additive for animals.

The hydrothermal processing of natural phosphates has been investigated under laboratory and semi-industrial conditions [47-53]. Two technological methods, applicable to different phosphate raw materials, have been developed. In the method developed for natural phosphates, not containing impurities and characterised by high temperatures of the onset of deformation and fusion, defluorination takes place in the solid phase. The main component of the apparatus used in this technological method is a rotating tubular furnace; to enhance the efficiency of the furnace, a process involving the granulation of the charge using phosphoric acid was developed.

The technological method for natural phosphates with impurities and low deformation and fusion temperature characteristics is based on the processing of the natural phosphate in the melt. Highly efficient cyclone furnaces were used in the fusion. The results were applied in industry. At the present time this process is being used in the Sumsk factory.

Recently Vol'fkovich has carried out interesting work at Moscow University and the Fertilisers, Insecticides, and Fungicides Institute on the problems of the chemistry and technology of dehydrated phosphates. The dehydrated phosphates (poly- and meta-phosphates) of ammonium and potassium are more concentrated in nutrient element content than the orthophosphate salts and may be used as highly effective concentrated fertilisers. Some of these salts are polymers which, depending on the physicochemical conditions, may be obtained in various polymeric modifications differing in composition and properties.

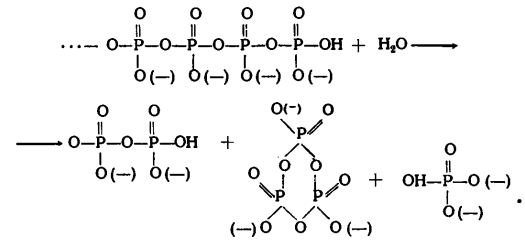
Vol'fkovich, Kubasova, Cherepanova, and others [54-56] investigated the methods for the preparation of potassium metaphosphate involving the reaction of polyphosphoric acids with potassium salts and thermal dehydration of acid salts of orthophosphoric acid; at the same time the structure and the physicochemical properties of the products were studied. A technological method, subsequently tested on a semi-industrial scale, was developed on the basis of laboratory experiments and a thermographic study of the dehydration of KH_2PO_4 to $(KPO_3)_n$, and also of the intermediates obtained in the decomposition of potassium chloride by orthophosphoric acid. Chemical and X-ray diffraction studies established the effect of small amounts of certain metal oxides on the structure of potassium metaphosphate. The relation between the structural characteristics of the specimens obtained and their solubility in water was determined.

Potassium polyphosphates obtained from polyphosphoric acids consist of a mixture of phosphates with a degree of condensation equivalent to several tens of phosphorus atoms in the chain. In contrast to high-molecular potassium polymetaphosphates of the composition $(KPO_3)_n$, these products exhibit high solubility in water and are therefore more completely and rapidly assimilated by plants.

Metal ammonium phosphates constitute an interesting class of compounds which are of practical importance. Vol'fkovich suggested that they be used as fertilisers. These compounds contain three nutrient elements — nitrogen, phosphorus, and the metal, and behave as concentrated fertilisers. They include magnesium, copper, manganese, and iron ammonium phosphates. They contain nitrogen in a sparingly soluble form. Some of the metal ammonium phosphates, in particular the aluminium and iron ammonium phosphates, can be used as insoluble fire-resistant materials. The idea that the metal ammonium phosphates be used as fire-resistant materials is due to Vol'fkovich and coworkers [57,58]. Later it was developed by his coworkers and applied in practice.

A number of Vol'kovich's studies dealt with the chemistry and technology of ammonium orthophosphates and polyphosphates. As early as the 1920's, the system $(NH_4)_2O-P_2O_5-SO_3-H_2O$ was investigated [59] and data necessary for the manufacture of Ammo-Phos were obtained. Aluminium phosphates are of very great theoretical and practical importance: since they contain two plant nutrient elements, they are widely used as concentrated and complex fertilisers. Dehydrated poly- and meta-phosphates are distinguished by a high content of nutrient elements and can be employed not only as fertilisers but also as components of wetting agents in certain bakery and technical chemical products. Dehydrated phosphates can be produced by direct reaction of P_2O_5 and NH_3, but the investigations of Britske and others showed that the formation of imido- and amido-groups is possible in this process.

In a study directed by Vol'fkovich, Kubasova [60] investigated the formation of dehydrated phosphates based on polyphosphoric acids; she investigated both the physicochemical properties and the structure of the compounds. The structure of the dehydrated phosphates was studied by X-ray diffraction analysis, infrared spectroscopy, thermography, chromatography, and other methods. These experiments showed that all water-soluble ammonium polyphosphates, obtained by the dehydration of monoammonium phosphate at 350°C, are amorphous to X-rays; an increase of the dehydration temperature results in the formation of sparingly soluble polyphosphates with crystalline as well as vitreous structures. The determination of the interplanar spacings in these crystals yielded values close to the lattice parameters of the kurrol sodium salt. The formation of the isotropic water-soluble modification is associated with the formation of ammonium phosphate glasses having the metaphosphate composition. To establish the nature of the P–O–P bond in the water-soluble ammonium polyphosphates, a study was made of their hydrolysis. These investigations showed that the hydrolysis of ammonium polyphosphates is similar to that of the polyphosphates of other cations and consists in the splitting of P–O–P bonds at the ends of long chains and the formation of trimetaphosphate rings, with a constant ratio $(P_3O_9):(PO_4) = 1:1$, by the following mechanism:



In this hydrolytic mechanism there are two OH groups for each trimeta- or ortho-phosphate group, of which only one is titrated at pH 8, namely the newly formed OH group at the end of the residual polyphosphate chain.

This mechanism suggests that the anions of the water-soluble ammonium polyphosphates have a linear chain structure, and this applies to all chain-type polyphosphates with a degree of condensation greater than five. The degree of dehydration and the average number of atoms in the chain were determined by the analysis of the terminal

functional groups by potentiometric titration. The infrared spectra of ammonium polyphosphates showed that, depending on the dehydration temperature, there is a decrease of the intensity of the bands characterising the P–OH bond upon condensation and an increase in the length of the polyphosphate chains. A technological method for the preparation of ammonium phosphates was developed on the basis of the experimental data.

Vol'fkovich and Urusov made a physicochemical study of the dehydration of ammonium orthophosphates and showed that ammonium metaphosphate may be prepared by heating the ortho-salt in an atmosphere of ammonia[61]. Vol'fkovich's studies on the synthesis of phosphoramidic and phosphorimidic acids are also of interest; according to Sokolov's agrochemical and vegetative experiments, some of these compounds are effective fertilisers which are not bound by the soil[62].

The rapid development of urea manufacture and the prospective manufacture of polyphosphoric acid open up new possibilities for the preparation of highly concentrated urea polyphosphate fertilisers which are of great interest for the mineral fertilisers industry. To develop their synthesis, Vol'fkovich and Chekhovskikh[63] made a physicochemical study of the system urea–polyphosphoric acid. This study was based on thermal and crystal-optical methods and visual observations over a range of temperatures. The molecular ratio of H_2O to P_2O_5 in the poly-acid was found to be 2.67 at a concentration of 74.5% P_2O_5 and 2.4 at 76% P_2O_5. These studies showed that in the system urea–polyphosphoric acid with R = 2.67 a 1 : 1 urea–polyphosphoric acid compound is formed. This compound melts congruently at 117.8–118°C and forms a eutectic with urea at 68°C and 64.5 mole % of urea and a peritectic with a second compound (2 : 1) which melts incongruently at 46°C. Polyphosphoric acid with R = 2.67 forms solid solutions, also with a eutectic corresponding to 15 mole % of urea. In the system urea–polyphosphoric acid with R = 2.462 a single 1 : 1 compound, melting congruently at 113°C, is also formed. This compound gives rise to a eutectic with urea at 74.8°C and 60 mole % of urea. The reaction between urea and polyphosphoric acids at a 1 : 1 molar ratio gave products containing 16.9–17.1% N and 51.6–52% P_2O_5, which may be used as fertilisers.

Vol'fkovich was the first Soviet scientist to investigate and apply industrially the electrothermal preparation of phosphorus from low-quality phosphorites native to the USSR [64,65] and he also made a series of studies [66–68] on the trapping and utilisation of fluorine-containing waste gases produced in natural phosphate processing, as a result of which the superphosphate factories of the Soviet Union have since produced a number of fluoride and fluorosilicate salts. In recent years he developed, together with members of the Fertilisers, Insecticides, and Fungicides Institute and factory workers, a synthesis of hydrofluoric acid from the gases evolved in phosphate mineral fertiliser factories. Vol'fkovich pioneered in the USSR the manufacture of hydrofluoric acid and fluoride salts from fluorspar. He and his coworkers were the first to investigate and develop methods of preparation of boric acid from borosilicate ores (datolites) and other materials [69–71], which until then had never been used as raw materials.

He made an extensive series of laboratory studies on the physicochemical conditions for the modification and improvement of the physical properties of ammonium nitrate[72,73], the preparation of ammonium sulphate from gypsum[74], and the reaction of sulphur dioxide with ammonia. He also carried out experiments on the chemical processing of potassium salts native to the USSR into chlorine-free potassium sulphate, phosphate, and nitrate fertilisers[74].

A characteristic feature of all of Vol'fkovich's research is endeavour to arrive at a manifold solution of the problem, permitting an almost complete utilisation of the available power and raw materials, and also to apply in chemical and technological research the facilities of modern technology and advanced methods of physical and physicochemical analysis. In his studies, he employed widely thermal, X-ray diffraction, spectroscopic, crystal-optical, chromatographic, isotopic, and other methods of research. To investigate the physical means of influencing chemical reactions, he has employed almost all the known advanced procedures, in particular those involving high-temperature catalytic processes in a fluidised bed and cyclone reactors.

Vol'fkovich proposed several substances (as well as methods for their manufacture) for the protection of plants and animals from pests and disease, and recommended a number of antiseptics for the protection of wood and certain organic materials from rot and decay. Vol'fkovich and coworkers synthesised a number of organic and organometallic substances. The relevent reactions include the synthesis of organophosphorus compounds by the interaction of phenol[75] with phosphorus and of phosphorus pentoxide with aluminium phenoxides[76], the preparation of melamine phosphates[77], the polycondensation of urea with various organic and inorganic compounds, the radiolysis of tetrachloroethylene and hexachlorobutadiene, and others[78]. Vol'fkovich is the author of the first technological method for the chemical manufacture of potassium chloride from Solikamsk potassium salts[79].

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DUAL REACTIVITY OF NITRO-COMPOUNDS IN ALKYLATION AND ACYLATION REACTIONS

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I. INTRODUCTION

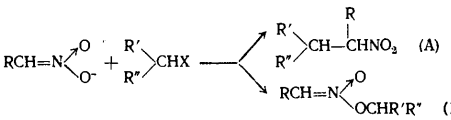
In recent years the scale of the studies on the chemistry of aliphatic nitro-compounds has been steadily increasing. Among the wide variety of the reactions which have attracted the attention of numerous investigators the alkylation and acylation of nitro-compounds merit attention. In the first place these reactions are of considerable theoretical interest since it is here that the dual reactivity of nitro-compounds is shown in a particularly pronounced form. Furthermore, they have attracted the attention of investigators for a long time as a method for preparing various nitro-derivatives and a wide variety of carbonyl compounds. However, despite the large number of studies on this problem, the available data have not been reviewed so far. The aim of the present review is to collect and compare the literature data on the alkylation and acylation of nitro-compounds with nitro-groups at saturated carbon atoms.

In the first section of the review the work done on the alkylation and acylation of mononitro-compounds, i.e. compounds with not more than one nitro-group at a single carbon atom, is considered. The second part deals with polynitro--compounds with several nitro-groups at a single carbon atom.

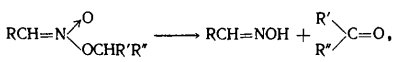
II. ALKYLATION AND ACYLATION OF MONONITRO--COMPOUNDS

1. Alkylation of *C*-Halogeno-Derivatives

In the alkylation of nitro-compounds their salts are employed as a rule. Consequently anions are actually involved in the reaction. Since the anions of nitro-compounds have two reaction centres (the oxygen of the nitro-group and the carbon bound to the latter), two modes of alkylation of nitro-compounds may be expected:

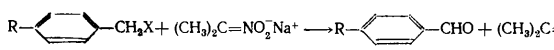


In the first case (*C*-alkylation) nitro-compounds are formed (A) while in the second case (*O*-alkylation) the products should be nitronic esters (B). As will be shown later, nitronic esters are as a rule unstable to heat and break down into a carbonyl compound and an oxime:



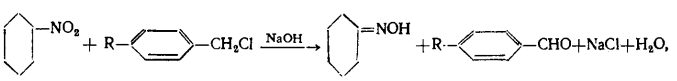
i.e. the breakdown of the ester involves intramolecular oxidation–reduction and ultimately the nitro-compound is reduced to the oxime and the halogeno-derivative is oxidised to the corresponding carbonyl compound.

The alkylation of mononitro-compounds has been studied in greatest detail in reactions with various halides of the benzyl type. In almost all cases such reactions results in alkylation of the oxygen only. Thus in the reactions with various *p*-substituted benzyl halides the sodium salt of 2-nitropropane yields only the corresponding benzaldehydes (in yields of 68–77%) and acetone oxime, i.e. the breakdown products of nitronic esters [1] †



where R = CH_3, Br, CH_3CO, CH_3OCO, CN, CF_3, $\overset{+}{N}(CH_3)_3I^-$.

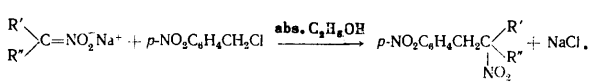
Similar results were obtained in the reactions of benzyl chloride with the potassium salt of 2-nitropropane [3], with the sodium salts of phenylnitromethane [4] and phenylnitroacetonitrile [4], and also with nitrocyclohexane [5]. The authors proposed the last reaction as a method for the preparation of alicyclic oximes and carbonyl compounds:



where R = H and CH_3.

The reaction of the silver salt of phenylnitroacetonitrile with benzyl chloride also gives an *O*-alkylation product [6].

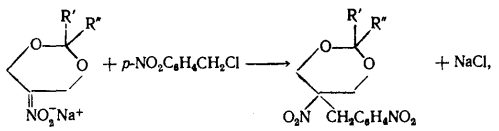
Among benzyl halides, *p*-nitrobenzyl chloride occupies an exceptional position, since, in contrast to all other benzyl halides, it alkylates alkali metal salts of nitroalkanes (nitroethane, 1- and 2-nitropropane, 1- and 2-nitrobutane, nitrocyclohexane, and nitrocyclopentane) almost exclusively at a carbon atom with formation of *p*-nitrophenyl-substituted nitroalkanes in yields between 30 and 60%: [7]



It is necessary to use a considerable excess of the nitroalkane, since otherwise polyalkylation products are formed [for example 1,1-bis-(*p*-nitrobenzyl)nitroethane may form from nitroethane [8]].

† The authors recommended this reaction as a general method for the synthesis of substituted benzaldehydes (see also Ref. 2).

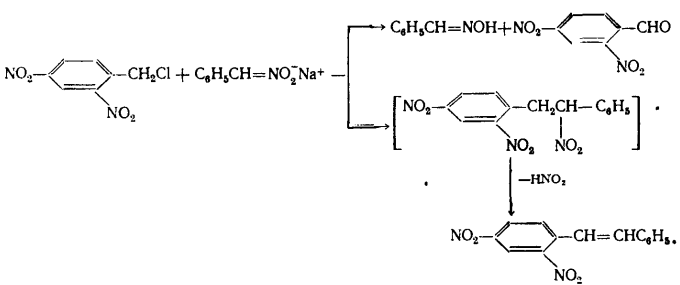
p-Nitrobenzyl chloride can also be successfully used for the *C*-alkylation of derivatives of 5-nitro-1,3-dioxan[9]:



where R′ = H and R″ = C_6H_5 (a) or R′ = R″ = CH_3 (b). In the reaction of this halide with the sodium salt of phenylnitromethane both *C*- and *O*-alkylation take place[4]. The mercury salt of phenylnitromethane does not enter into a similar reaction[4].

When *p*-nitrobenzyl halides are allowed to react with salts (sodium and silver) of phenylnitroacetonitrile, only the oxygen is alkylated[4]. It has been stated that *o*-nitrobenzyl chloride gives bis-(*o*-nitrobenzyl)nitromethane on reacting with the sodium salt of nitromethane[10], but the yield has not been given.

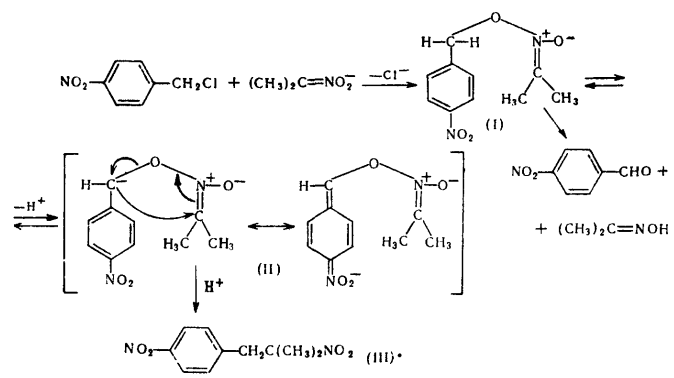
2,4-Dinitrobenzyl chloride and the sodium salt of phenylnitromethane yield both *O*- and *C*-derivatives. However, in the latter case, the product is unstable and breaks down to give 2,4-dinitrostilbene[4]:



C-Alkylation takes place in the reaction of 2,4-dinitrobenzyl chloride with the sodium salt of 2-nitropropane (yield 33%)[11].

The above data show that in the alkylation of the salts of nitroalkanes with benzyl halides it is virtually only *p*-nitrobenzyl chloride that gives products of alkylation exclusively at the carbon atom; in all the remaining cases *O*-alkylated derivatives are almost the only products. This is seen particularly clearly in the following example: in the reaction of the sodium salt of 2-nitropropane with nitro-substituted benzyl chlorides the *para*-isomer gives only *C*-alkylated products (yield 83%), the *ortho*-isomer gives products corresponding to 46% *C*-alkylation and 30% *O*-alkylation, while the *meta*-isomer and the unsubstituted benzyl chloride give rise to *O*-alkylation alone (in 73% yield)[11].

The study of the kinetics of the reaction of the lithium salt of 2-nitropropane with *o*-, *m*-, and *p*-nitrobenzyl chlorides (in ethanol at 30°) showed that the reaction is of the second order and its rate is approximately the same as that of the reaction of potassium iodide (in acetone) with the same halides[11]. Hass and Bender[11] put forward the following mechanism for the reaction of the salts of nitroalkanes with benzyl halides: both in *O*- and in *C*-alkylation the initial stage is alkylation of the oxygen with formation of the nitronic ester (I) which then either breaks down into an aldehyde and an oxime or ionises to give a resonance-stabilised carbanion (II). As a result of intramolecular rearrangement the latter then yields the *C*-alkylation product (III):



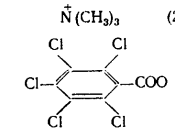
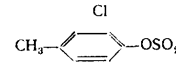
The presence of a nitro-group in the *para*-position of the benzyl ring greatly facilitates the removal of a proton from compound (I) and thereby leads to complete conversion of (I) into (II), i.e. ultimately to *C*-alkylation.

However, this mechanism does not explain why the mode of alkylation depends on the nature of the group being substituted in the *p*-nitrobenzyl system. Thus Kornblum and coworkers[12,13] showed that in the reaction of the lithium salt of 2-nitropropane with various *p*-nitrobenzyl derivatives the ratio of the products of *C*- and *O*-alkylation varies sharply with the group being substituted (see Table).

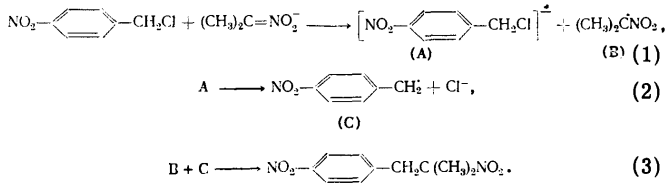
Another argument against the mechanism of Hass and Bender[11] was adduced by Boyd and Kelly[14], who showed that in the *C*-alkylation of nitro-compounds with allyl halides there is no allyl rearrangement which would have to take place if Hass and Bender's hypothesis of the initial formation of *O*-alkylation products and their subsequent rearrangement to *C*-alkylation products were correct.

Recently Kornblum and coworkers[15] suggested a new alkylation mechanism to account for the specificity of the reactions of nitroalkane salts with *p*-nitrobenzyl derivatives. They believe that, whereas *O*-alkylation involves the usual nucleophilic substitution at the oxygen atom of the

TABLE. Mode of reaction of p-$NO_2C_6H_4CH_2X$ with the lithium salt of 2-nitropropane (in dimethylformamide at -16°) depending on the nature of X.[12,13]

X	C-Alkylation, %	O-Alkylation, %
$\overset{+}{N}(CH_3)_3$ (25°)	93	0
	93	0
Cl	95	1
	40	32
Br	17	65
I	7—9	81

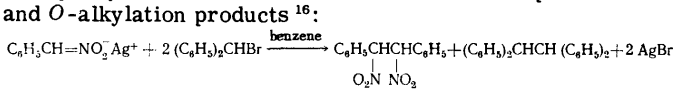
nitro-group, *C*-alkylation is a more complex anionic-radical process:



In this mechanism the first stage of the reaction consists in the transfer of an electron from the nitroalkane anion to the aromatic system [Eqn. (1)], this being followed by the loss of a chloride ion by the radical-anion (A) [Eqn. (2)] and the recombination of the two radicals (B) and (C) [Eqn. (3)].

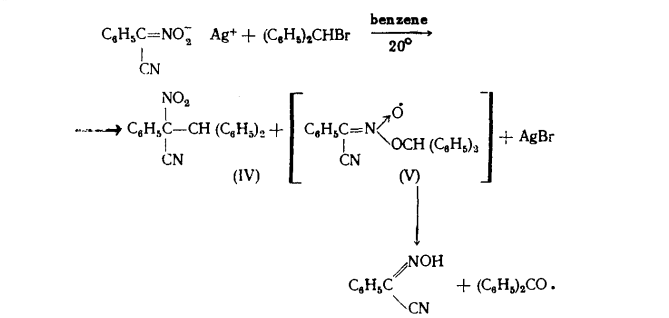
This hypothesis is based on the study of alkylation kinetics [15] (the slight increase of the rate of *C*-alkylation on going from *p*-nitrobenzyl chloride to the bromide and then the iodide, which is untypical for an S_N2-process) and was confirmed by the detection of radical-anions in the reaction mixture (by the ESR method).

The reactions of mononitro-compounds with α-phenyl substituted benzyl halides and with di- and tri-phenyl halogenomethanes are more complex. Thus in the reaction of the silver salt of phenylnitromethane with diphenylbromomethane, 1,2-diphenyl-1,2-dinitroethane and the symmetrical tetraphenylethane are obtained instead of the expected *C*- and *O*-alkylation products [16]:

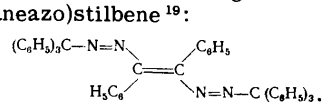


The authors believe that the unstable silver salt of phenylnitromethane breaks down with formation of diphenyldinitroethane and silver, the latter reacting with the initial bromide to give tetraphenylethane.

The reaction of the silver salt of phenylnitroacetonitrile gives, although in low yield, the *C*-alkylation product — triphenylnitropropionitrile (IV). [17] However, it was shown subsequently [18] that the principal mode of this reaction is *O*-alkylation with formation of the nitronic ester (V) which decomposes into α-isonitrosobenzyl cyanide and benzophenone:

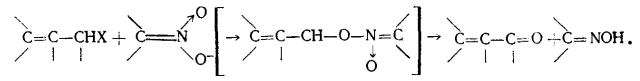


The reaction of triphenylchloromethane with the mercury salt of phenylnitromethane gives the *C*-alkylation product, 1,1,1,2-tetraphenyl-2-nitroethane, in 33–40% yield [4,17]. The reaction of triphenylchloromethane with the silver salt of phenylnitroacetonitrile is much more complex [17,19]. Initially it was believed that the *C*-alkylation product is formed [17], but later it was shown that the reaction gives rise to αα′-bis-(triphenylmethaneazo)stilbene [19]:



In addition, it proved possible to isolate triphenylmethyl isocyanate and a compound of unknown structure [19] with the empirical formula $C_{14}H_{11}N_{13}O$.

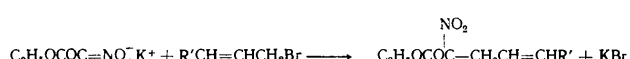
Halides of the allyl type, whose reactivity is similar to that of benzyl halides, alkylate mononitro-compounds at the oxygen atom as a rule. Thus the reaction of alkali metal salts of nitroalkanes with a series of allyl halides of different structures containing one or two allylic halogen atoms, gives rise to αβ-unsaturated mono- and di-aldehydes or ketones as a result of the breakdown of the intermediate nitronic esters [20]:



Both primary and secondary nitroalkanes and primary and secondary allyl bromides and chlorides may be used in the reaction (best results were obtained with the salts of 2-nitropropane [20] and nitrocyclohexane [21]). This reaction serves as a basis for the preparative synthesis of unsaturated aldehydes, for example citral and its homologues [21,22], which are used in the manufacture of perfumes.

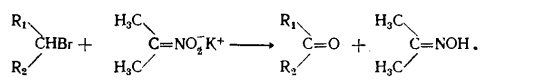
O-Alkylation is also achieved with the aid of a cyclic halide of the allyl type, 3-bromocyclohexene, which reacts with the sodium salt of 2-nitropropane with formation of an unsaturated ketone (cyclohexenone) and acetone oxime [23]. Another product is cyclohexadiene (formed by the dehydrohalogenation of the initial bromide).

Mononitro-compounds have been alkylated at the carbon atom by allyl halide in only a few cases. Thus the reaction of the salts of nitroacetic and nitromalonic esters with allyl halides gives small yields (10–30%) of the corresponding *C*-derivatives [14] ‡:



where R = H and C_2H_5OCO and R′ = H and CH_3.

Many investigators have studied the alkylation of various mononitro-compounds with alkyl halides. In almost all cases the oxygen atom was alkylated with formation of nitronic esters (sometimes isolated in a pure form) or their decomposition products. The potassium salt of 2-nitropropane reacts with various alkyl halides (undecyl and dodecyl bromide, 1-piperonyl-2-bromoethane, and others) with formation of aldehydes and acetone oxime [3]:

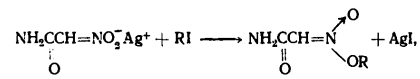


The corresponding oxime is also formed in the reaction of the sodium salt of 1,1,2-triphenyl-2-nitroethane with methyl iodide [25]. When the potassium salt of 9-nitrofluorene reacts with alkyl halides, fluorenone oxime is formed and also the corresponding aldehyde, ketone, or olefin, depending on the nature of the halide (primary, secondary, or tertiary) [26]. Similar results were obtained with the silver salt of 2-bromo-9-nitrofluorene [27].

The reaction of the sodium salt of phenyl- and *p*-bromophenylnitromethane with methyl iodide is unusual, the products being stilbene (or 4,4′-dibromostilbene) and

‡ In a paper published in 1873 [24] an attempt to synthesise 4-nitropent-1-ene from the potassium salt of nitroethane and allyl iodide is described; however, the reaction product was not identified.

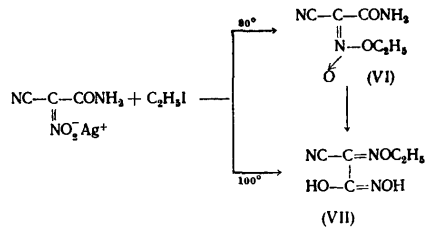
benzaldehyde[26]. The reaction of the sodium salt of phenylnitromethane with t-butyl bromide gives only the free phenylnitromethane[26]. In many cases stable nitronic esters, resulting from *O*-alkylation, can be isolated when alkyl halides react with salts of mononitro-compounds. Such esters were obtained, for example, in the reaction of the silver salt of nitroacetamide with various alkyl iodides[28,29]:



where R = CH_3, C_2H_5, n-C_3H_7, and iso-C_5H_{11}. The silver salt of the diamide of nitromalonic acid does not enter into a similar reaction[30].

When the silver salt of phenylnitroacetonitrile reacts with methyl iodide, it is possible to isolate a relatively stable nitronic ester[6,31]; in another study only the decomposition product of this ester, an oxime, was obtained[32]. The results of the reaction of *p*-bromophenylnitroacetonitrile were similar[33].

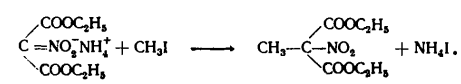
The reaction of the silver salt of fulminic acid (cyanonitroacetamide) with ethyl iodide also gives a nitronic ester (VI),[34] or, at a higher temperature, its rearrangement product (VII):[35,36]



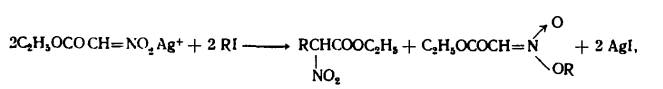
(VII)

A stable nitronic ester was obtained from the silver salt of 3-methyl-4-nitro-5-iso-oxazolone and ethyl iodide[37].

Only a few examples of *C*-alkylation of mononitro-compounds with alkyl halides are known. Thus α-methyl-α--nitromalonic ester is formed in the reaction between methyl iodide and ammonium nitromalonate[38]:

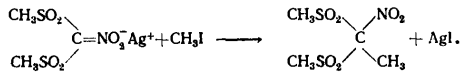


However, when ethyl iodide is used, let alone other alkyl halides, the reaction proceeds with considerable difficulty[39]. The reaction of the sodium salt of 2-chloro-2-nitroethanol with methyl iodide also yields a *C*-alkylation product[40] — 2-chloro-2-nitro-1-propanol (yield not stated)[40]. The silver salt of nitroacetic ester reacts with alkyl iodides with formation of both *O*- and *C*-alkylation products (the yield of the latter is 20–25%)[41]:



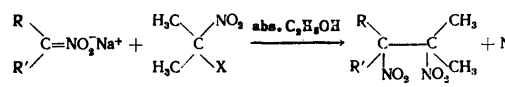
where R = CH_3 and C_2H_5. Alkyl bromides do not enter into this reaction[41].

There exist also patent data on the preparation of *C*-derivatives by the alkylation of nitromalonic ester with alkyl halides and also other alkylating agents (sulphites, sulphonates, and others), but the details of the experimental procedure are not indicated[42]. Backer[43] mentions the *C*-alkylation of the silver salt of bis(methylsulphonyl)nitromethane with methyl iodide but the yield of the product was very low:



It is also interesting that the reaction of 1-(*p*-nitrophenyl)--2-bromoethane with the sodium salt of 2-nitropropane results in alkylation at the carbon atom with formation of 3-methyl-3-nitro-1-(*p*-nitrophenyl)butane (yield 54%)[11].

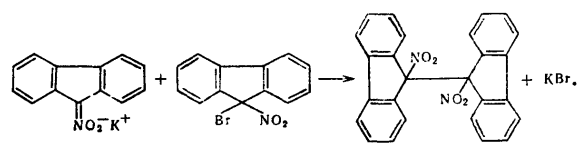
Seigle and Hass[44,45] showed that the reaction of alkali metal salts of secondary nitroalkanes with halogenonitro--compounds in which the halogen and the nitro-group are attached to the same carbon atom yields vicinal dinitroalkanes:



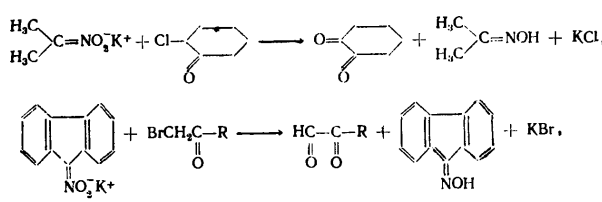
where R and R′ = CH_3, C_2H_5, and $-(CH_2)_5-$, and X = Cl, Br, and I. The yields of the *C*-alkylation products are 10% for the chloride, 20–30% for the bromide, and 43% for the iodide§.

Primary nitro-compounds do not enter into this reaction as a rule[44]; however, Nenitzescu and Isacescu[26] succeeded in obtaining 1,2-diphenyl-1,2-dinitroethane by allowing the sodium salt of phenylnitromethane to react with phenyliodonitromethane. The salts of *p*-bromo- and *p*-methyl--phenylnitromethanes do not react with this iodide[26].

The potassium salt of 9-nitrofluorene reacts with 9-bromo-9-nitrofluorene to give 1,2-di(biphenylene)-1,2--dinitroethane[26]:



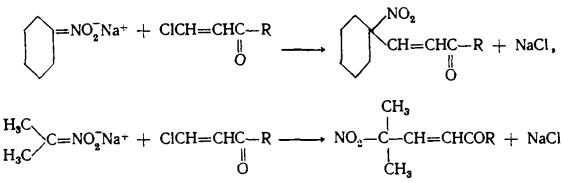
Of the other halogeno-derivatives which react with mononitro-compounds, halogeno-ketones should be mentioned. Thus the reaction of the potassium salt of 2-nitropropane with 2-chlorocyclohexanone[3] gave 1,2-cyclohexadione, while the reaction of the potassium salt of 9-nitrofluorene with bromoacetone and ω-bromoacetophenone resulted in the formation of methyl- and phenyl-glyoxal respectively (in yields of 85–95%) and fluorenone oxime[47]:



where R = CH_3 and C_6H_5.

§ Later it was shown that the yield of nitroalkanes depends significantly on the purity of the initial nitro-compounds: thus when pure 2-nitropropane is used, it is possible to increase the yield of 2,3-dimethyl-2,3-dinitrobutane to 50% for the chloride and to 80% for the bromide[46].

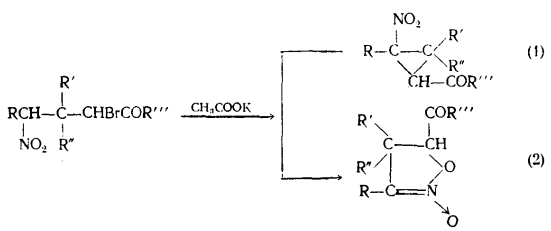
Only rather unusual halogeno-ketones, such as β-chlorovinyl ketones, alkylate nitro-compounds at the carbon atom, and even then as a rule with low yields[48-50]:



where R = CH_3, C_2H_5, n-C_3H_7, C_6H_5, p-$CH_3C_6H_4$, p-ClC_6H_4, and p-BrC_6H_4.

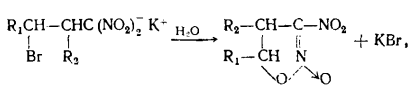
An attempt to condense the potassium salt of nitroethane with iodoacetic ester was unsuccessful[51]. Chloroacetic ester reacted with the potassium salt of 9-nitrofluorene to give fluorenone oxime and ethyl glyoxylate[26].

An unusual type of alkylation of nitro-compounds has been described in a number of papers of Kohler, Smith, and others. They showed that, when compounds of the type RCH(NO_2)CR'R"CHBrCOR'", containing a halogen in the γ-position with respect to the nitro-group and in the α-position with respect to the carbonyl, are heated with potassium acetate, intramolecular alkylation takes place with formation of either cyclopropane derivatives (*C*-alkylation)[52-58] or isoxazoline oxides (*O*-alkylation)[59-64]:



The formation of nitrocyclopropanes [reaction (1)] occurs only when primary nitro-compounds are used (R = H); secondary nitro-compounds give only the *O*-alkylation products [reaction (2)].[62]

Tartakovskii et al. showed recently[65] that, when two nitro-groups are present in the γ-position with respect to halogen, only *O*-alkylation takes place, *N*-oxides of nitroisoxazolines being formed¶:



where R_1 = H and CH_3OCO, R_2 = H, CH_3, and C_6H_5, and R_1-R_2 = -$(CH_2)_3$- and -$(CH_2)_4$-.

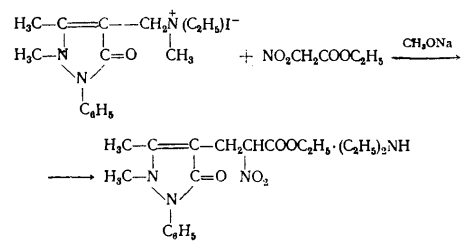
2. Alkylation with Mannich Bases and Quaternary Ammonium Bases

Alkylation with Mannich bases is known to take place according to one of two mechanisms (see, for example, Hellman and Opitz[67]): the so-called "elimination-addition" mechanism or the nucleophilic substitution mechanism.

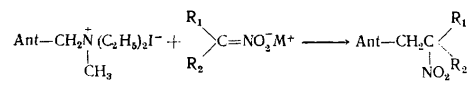
All tertiary Mannich bases with even only one labile hydrogen atom in the β-position with respect to the nitrogen (or the vinylogues of such bases) alkylate according to the first of the above mechanisms, which comprises two stages: (a) elimination of the amine from the Mannich base with formation of an unsaturated compound and (b) the Michael addition of the component to be alkylated to the unsaturated compound.

In the present review we shall consider the alkylation of mononitro-compounds only by Mannich bases which are incapable of alkylation by the above mechanism, i.e. those that react according to the nucleophilic substitution mechanism. This reaction is successful only in those cases where quaternary ammonium salts of Mannich bases incapable of undergoing deamination are used, since after removal of the tertiary amine, the bases form a carbonium ion stabilised by electron delocalisation and capable of reacting with the anion of the nitro-compound to be alkylated[67].

For example, 2-nitropropane is not alkylated by dimethyl-(β-nitroisobutyl)amine[68]. Also there is no alkylation when nitroacetic ester reacts with the tertiary Mannich base derived from antipyrine[69]†. On the other hand, when a quaternary salt, the methiodide of diethylaminomethylantipyrine, is used, nitroacetic ester can be alkylated with a 48% yield[71]:

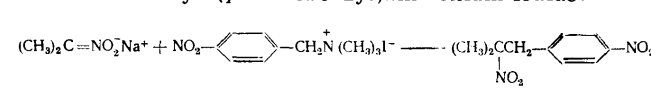


The alkylation of the potassium salt of the anilide of nitroacetic ester[71] and the sodium salt of nitromalonic ester takes place similarly[69]:



where R_1 = H and R_2 = $CONHC_6H_5$ or R_1 = R_2 = $COOC_2H_5$; M = Na and K, and Ant = antipyrine residue. The methiodide of 1-dimethylamino-2-methyl-2-nitropropane (Mannich base derived from nitropropane) proved to be unsuitable for *C*-alkylation of nitro-compounds[68].

Several examples of related reactions, the alkylation of the salts of mononitro-compounds with quaternary ammonium bases, have been described. Thus Schechter and Kaplan[72] obtained a 63% yield of the corresponding *C*-alkylation products by allowing the sodium salt of 2-nitropropane to react with trimethyl-(p-nitrobenzyl)ammonium iodide:

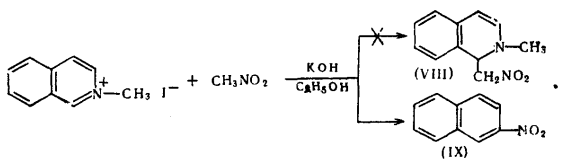


In the absence of the p-nitro-group in the phenyl ring, only benzaldehyde is formed[72], i.e. only *O*-alkylation takes place.

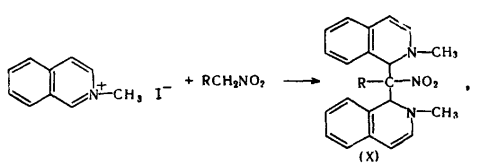
¶ A recent communication[66] described the conversion of the potassium salt of β-bromoethyl dinitroacetate, on boiling in acetone, into αα-dinitro-γ-butyrolacetone, i.e. intramolecular *C*-alkylation with formation of a five-membered ring takes place.

† The assertion by Dornow and Thies[70] that alkylation does occur in this case proved to be incorrect; in fact only the salt of one of the initial reaction components is formed[69].

The reaction of nitroalkanes with quaternary quinolinium and isoquinolinium salts is unusual. When nitromethane reacts with the methiodide of isoquinoline, 2-nitronaphthalene (IX) is obtained instead of the expected product (VIII):[73]

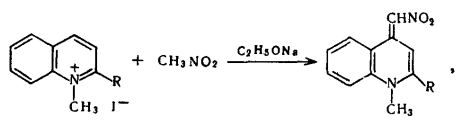


Under similar conditions nitroethane and 1-nitropropane give only bis-[1-(2'-methyl-1',2'-dihydroisoquinolyl)]-nitroalkanes (X):[73]



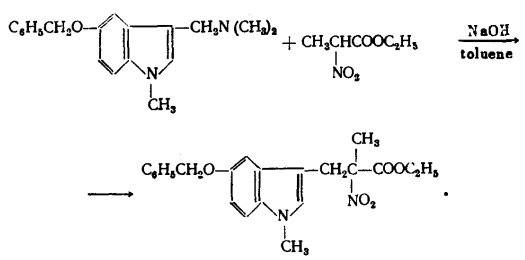
where R = CH_3 and C_2H_5. In addition to compound (IX), nitromethane also gives a small compound of compound (X) (R = H).[73]

The reaction of nitromethane with quinolinium or 2-methylquinolinium methiodide takes place in a different manner — with formation of 1-methyl-4-nitromethylenequinolanes:

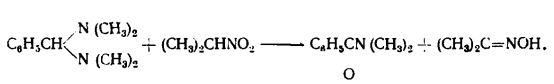


where R = H and CH_3. The reaction does not occur when a substituent is present in position 4 of the quinoline ring[74].

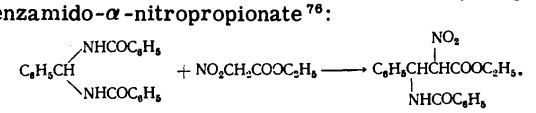
Only one example of the alkylation of nitro-compounds with a tertiary Mannich base (incapable of being deaminated), of the *N*-methylgramine series, is known. When 5-benzyloxy-1-methylgramine reacts with nitropropionic ester in the presence of sodium hydroxide, the desired alkylation product is formed in 14% yield[75]:



In this section it is also appropriate to mention the alkylation of mononitro-compounds with *N*-substituted benzylidenebisamines. Thus *NN'*-benzylidenebisdimethylamine reacts with 2-nitropropane to give a mixture of benzoic acid dimethylamide and acetone oxime[3]:

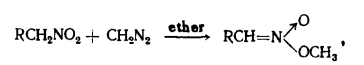


The author explains this reaction by the decomposition of the nitronic ester formed as an intermediate as a result of *O*-alkylation. Similar results were also obtained with benzylidenebispiperidine[3]. On the other hand, the reaction of nitroacetic ester with *NN'*-benzylidenebisbenzamide results only in *C*-alkylation with formation of ethyl β-phenyl-β-benzamido-α-nitropropionate[76]:



3. Alkylation with Other Alkylating Agents

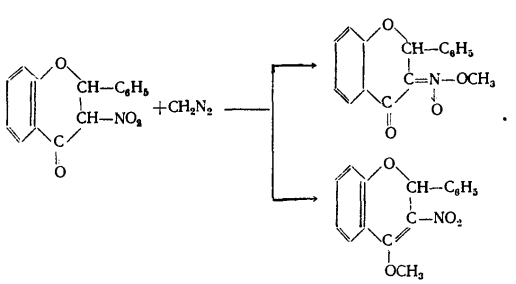
Apart from the alkylating agents enumerated above, a number of others are used in reactions with mononitro-compounds (diazomethane, dimethyl sulphate, olefin oxides, and others). With a few exceptions, the alkylation always involves the formation of nitronic esters or products of their further reaction. Thus a number of workers have shown[77,78,80,81] that diazomethane can be successfully used for the *O*-alkylation of nitro-compounds. Arndt and Rose[77], who studied the behaviour of nitro-compounds of different types in the reaction with diazomethane, concluded that the more acidic is the nitro-compound the more readily it is alkylated by diazomethane:



where R = C_6H_5, *p*-BrC_6H_4, C_6H_5CO, C_2H_5OCO, *p*-$CH_3C_6H_4SO_2$, etc.

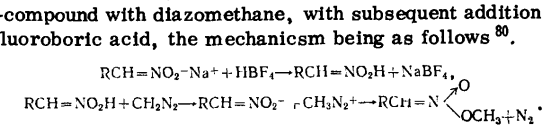
While phenylnitromethane reacts with diazomethane over a period of three days, the reaction with nitroacetic ester is completed in 2 h and that with nitromalonic ester is practically instantaneous. The reaction of diazomethane with *aci*-nitro-compounds is even faster than with true nitro-compounds[77].

It has recently been shown that the cyclic α-nitro-ketone 3-nitroflavanone is readily alkylated by diazomethane[78], yielding a mixture of two products — a nitronic ester and the ester of the enol form of the initial ketone:

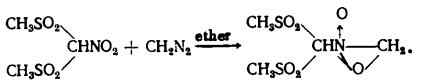


It is noteworthy that the nitro-compounds which are relatively weak acids (for example, nitromethane[79] and 1-phenyl-3-nitropropane[80]) do not enter into this reaction‡.

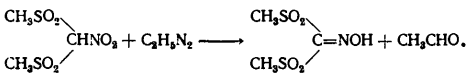
‡ The difficulty of alkylating compounds of this kind, which is probably due to the low rate of proton transfer from the nitro-compound to diazomethane, can be overcome by treating a salt of the nitro-compound with diazomethane, with subsequent addition of tetrafluoroboric acid, the mechanicsm being as follows[80].



The reaction of diazomethane with bis(methylsulphonyl)-nitromethane also results in *O*-alkylation with formation (in quantitative yield) of a nitronic ester which, according to the author, is the *N*-oxide of *N*-[bis(methylsulphonyl)-methyl]epoxymethyleneimine [81]:

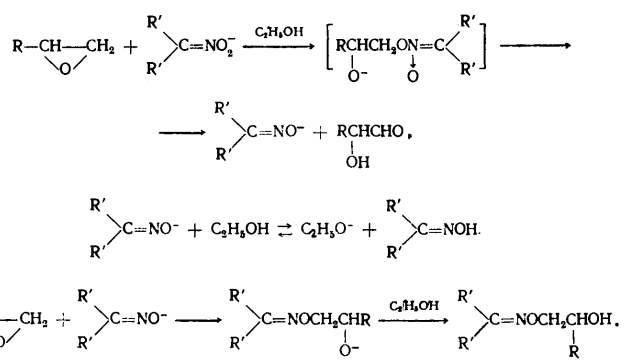


After the reaction of bis(methylsulphonyl)nitromethane with diazoethane, the same investigator [81] was able to isolate only the decomposition products of the *O*-nitronic ester — bis(methylsulphonyl)isonitrosomethane and acetaldehyde:



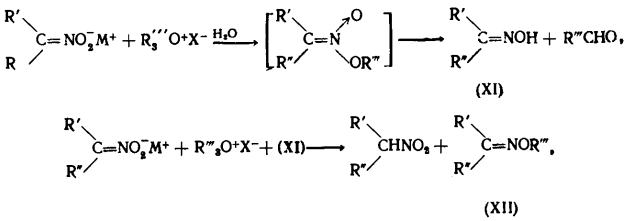
A nitronic ester is also formed when phenylnitromethane (in the form of the sodium salt) is alkylated with dimethyl sulphate [77,82]. The reaction of dimethyl sulphate with the potassium salt of 9-nitrofluorene is similar [83]: it yields a nitronic ester which decomposes to fluorenone oxime and formaldehyde on raising the temperature.

Bachman and Hokama [84] introduced into the reaction with nitroalkanes various olefin oxides (ethylene, propene, and styrene oxides) in an alkaline medium (in the presence of lithium alkoxide) and obtained only the oximes and the oxime ethers whose formation they regard as due to *O*-alkylation followed by decomposition of the reaction products into the carbonyl compounds and the oxime:



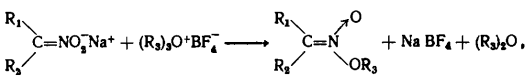
In another study on the alkylation of nitro-compounds by olefin oxides [85] the latter were introduced into the reaction with various mononitroalkanes in pyridine solution. The reactions are very complex, the corresponding γ-nitro--alcohols (*C*-alkylation products) either not forming at all or their yield not exceeding several per cent. The main products are 1-(2′-hydroxyalkyl)pyridinium nitrites and 3,4,5-trimethoxyisoxazole from primary nitroalkanes, while secondary nitroalkanes give in addition vicinal dinitroalkanes, ketones, and ketone oximes.

The reaction of the salts of mononitro-compounds with rather unusual alkylating agents such as trialkyloxonium salts has been investigated in fair detail. Thus Donaruma [86] allowed salts of nitrocyclohexane, nitrocyclopentane, and 2-nitropropane to react with trialkyloxonium fluoroborates, chloroferrates, and chloroaluminates, and in all cases observed the formation of *O*-alkylation products — oximes (XI) and the *O*-alkylated oximes (XII) (ethers):



where R′ and R″ = $-(CH_2)_4-$, $-(CH_2)_5-$, and CH_3, R‴ = = CH_3 and C_2H_5, X = BF_4, $FeCl_4$, and $AlCl_4$, and M = Na and K. The best yields of oximes (50–80%) and their ethers (20–35%) are obtained when trialkyloxonium fluoroborates are used, particularly when R‴ = C_2H_5; triethyloxonium chloroferrate and chloroaluminate react to a much smaller extent, due to side-processes (in particular due to the formation of sparingly soluble iron and aluminium salts of the nitroalkanes by double decomposition with ferric chloride and aluminium chloride, the salts being precipitated during the alkylation).

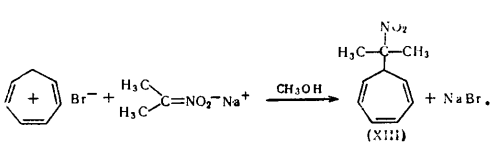
Quite recently Kornblum and Brown [80,87] used the reaction with trimethyl- and triethyl-oxonium fluoroborates to prepare nitronic esters from many aliphatic and aliphatic–aromatic mononitro-compounds:



where R_1 = CH_3, n-C_3H_7, *p*-BrC_6H_4, and *p*-$NO_2C_6H_4$, R_2 = = H and CH_3, and R_3 = CH_3 and C_2H_5. The reaction was carried out in methylene chloride at 0°, the yield of the esters being very high (80–95%). It is noteworthy that the nitronic esters from purely aliphatic nitro-compounds had not been isolated before this study.

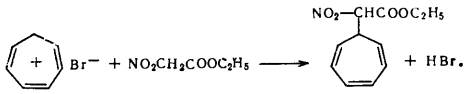
There are patent data on the alkylation of salts of primary or secondary aliphatic and alicyclic nitro-compounds with alcohols and phenols in neutral or acid media [88], the reaction resulting in *O*-alkylation with formation of oximes. The reaction can also be carried out in the presence of ammonia, amines, or ammonium salts.

Interesting results were obtained in the alkylation of nitro-compounds with tropylium bromide. Thus by allowing tropylium bromide to react with the sodium salt of 2-nitropropane, Bersohn [23] obtained a high yield (68%) of the *C*-alkylation product — 1-(dimethylnitromethyl)cyclohepta--2,4,6-triene (XIII):

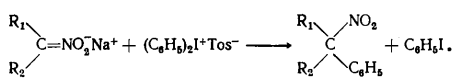


He believes [23] that initially the *O*-alkylation product forms and then readily dissociates into the initial ions with subsequent formation of the thermodynamically stable *C*-alkylation product. This process is much faster than the usual breakdown of nitronic esters into the oxime and the carbonyl compound and therefore the *C*-alkylation derivative gradually accumulates: *O*-alkylation products were not detected in this reaction.

The alkylation of nitroacetic ester with tropylium bromide takes place in exactly the same way, the only product being ethyl cycloheptatrienylnitroacetate[89]:

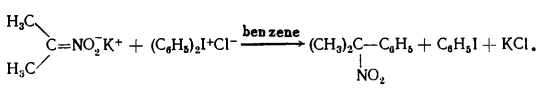


Yet another case of *C*-alkylation (more precisely arylation) of nitro-compounds was described recently by Kornblum and Taylor[90]: by allowing salts of primary and secondary nitroalkanes to react with diphenyliodonium toluenesulphonate in dimethylformamide, they obtained a good yield (55–70%) of the corresponding phenylnitroalkanes:



where $R_1 = CH_3$, $n\text{-}C_3H_7$, and $n\text{-}C_7H_{15}$, $R_2 = H$ and CH_3, and $R_1\text{–}R_2 = -(CH_2)_5-$.

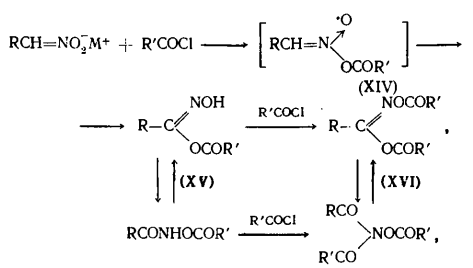
It proved impossible to make the potassium salt of phenylnitromethane undergo a similar reaction[91]. Diphenyliodonium chloride can be used successfully instead of the toluenesulphonate; the potassium salt of 2-nitropropane is then converted into 2-phenyl-2-nitropropane in 63% yield[92]:



4. Acylation of Mononitro-Compounds

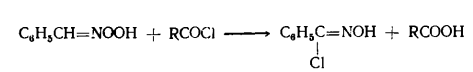
Much less attention has been given in the literature to the acylation of mononitro-compounds than to their alkylation. However, here too various acylating agents have been investigated — acyl halides, acid anhydrides, ketene, acyl cyanides, and others. In almost all cases *O*-acylation takes place exclusively with formation of nitronic acid anhydrides which then as a rule undergo further reactions.

The acylation of mononitro-compounds by acyl halides has been studied in greatest detail. Thus the reactions of salts of primary nitroalkanes with acetyl chloride and benzoyl chloride yield various acylhydroxamic acids, (XV) and (XVI), the products of the rearrangement of the anhydrides (XIV) and subsequent repeated acylation[93–95]:



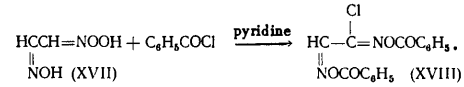
where R = H and CH_3 and R′ = CH_3 and C_6H_5.

Similar results were obtained in the acylation of the sodium salts of arylnitromethanes[83,96,97]. The acylation of *aci*-phenylnitromethane yields the chloride of benzohydroxamic acid[83]:

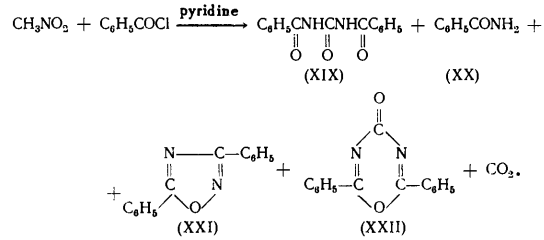


where R = CH_3 and C_6H_5. In many cases no products could be identified after the reaction of primary nitroalkanes with acyl halides[98–100].

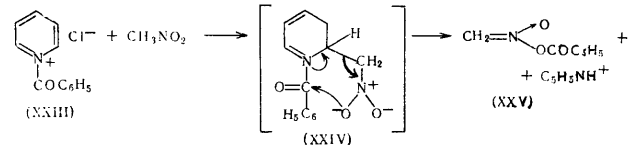
The acylation of primary mononitro-compounds by acid chlorides in pyridine solution is unusual. Thus in the reaction of phenylnitromethane and ω-nitroacetophenone with benzoyl chloride in pyridine the main product is in both cases dibenzohydroxamic acid ($C_6H_5CONHOCOC_6H_5$).[101] On the other hand, when *aci*-phenylnitromethane is used in a similar reaction, the product is the chloride of benzoylbenzohydroxamic acid ($C_6H_5CCl{=}NOCOC_6H_5$).[102] Under the same conditions methazonic acid (XVII) gives dibenzoylchloroglyoxime (XVIII):[102]



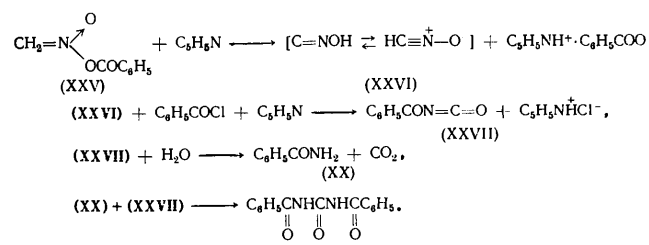
The reaction of benzoyl chloride with nitromethane in pyridine solution is much more complex[101]. It proceeds with evolution of carbon dioxide and the formation of *NN′*-dibenzoylurea (XIX) as the main product; in addition benzamide (XX), benzonitrile, 3,5-diphenyl-1,2,4-oxadiazole (XXI), and a substance with the empirical formula $C_{15}H_{10}N_2O_2$, possibly 2,6-diphenyl-4-oxo-1,3,5-oxadiazine (XXII), were isolated from the reaction mixture:



The authors of this investigation believe that in this case the acylating agent is benzoylpyridinium chloride (XXIII) which initially combines with nitromethane to give an intermediate (XXIV), and the latter then decomposes into the mixed anhydride (XXV):



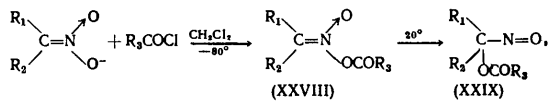
To account for the formation of *NN′*-dibenzoylurea (XIX), the authors proposed further the following mechanism:



The reasons for the formation of the other products are obscure. It is interesting that, on replacing pyridine by quinoline or dimethylaniline, not even traces of compound (XIX) are formed[101].

The acylation of secondary mononitro-compounds by acyl halides has been investigated in greatest detail by White and

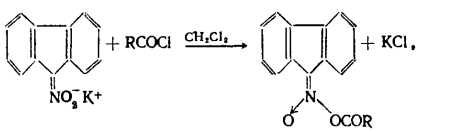
Considine [103,104]. They found that the initial products of the reactions of salts of secondary nitroalkanes with acid chlorides are the anhydrides (XXVIII), as in the case of other mononitro-compounds. On raising the temperature of the reaction mixture, a pale blue colour gradually appears, due to the extremely ready isomerisation of the nitronic anhydrides to nitrosoacyloxy-compounds (XXIX) [104] §:



(XXVIII) (XXIX)

where R_1 and R_2 = CH_3, C_6H_5, and $-(CH_2)_5-$ and R_3 = CH_3, C_6H_5, and p-$NO_2C_6H_4$. The authors were unable to obtain C-acylation products; judging from the infrared spectra, the latter are formed in amounts smaller than 1%.

In some cases on acylating secondary nitro-compounds with acyl halides it proved possible to isolate stable nitronic esters. Thus Nenitzescu and Isacescu [83] obtained O-acetyl and O-benzoyl-9-*aci*-nitrofluorenes (XXX) by allowing the potassium salt of 9-nitrofluorene to react with acetyl and benzoyl chlorides respectively:



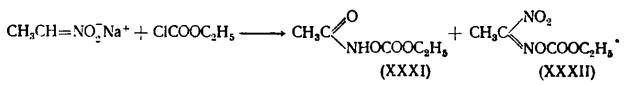
(XXX)

where R = CH_3 and C_6H_5. Subsequently White and Considine [103] confirmed the structure of compound (XXX) (R = = C_6H_5).

Another interesting case of the formation of a stable nitronic anhydride has been described by Thurston and Shriner [6]: when the sodium or silver salt of phenylnitroacetonitrile was treated with benzoyl chloride, O-benzoyl-*aci*-nitrophenylacetonitrile was obtained:

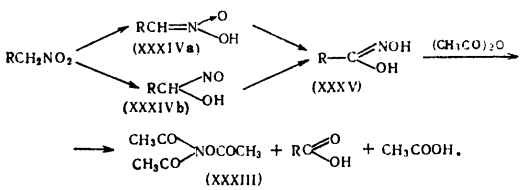
where M = Na and Ag. The authors demonstrated the structure of the product and thereby disproved the assertion of Wieland and Höchtlen [17] that they isolated the C-benzoyl derivative in a similar reaction with benzoyl bromide¶. According to Foster's data [107], the reaction of 1-nitrobornane with benzoyl chloride also yields a stable nitronic anhydride, but the product was not characterised.

The use of the ethyl ester chlorocarbonic acid as the acylating agent has been as a rule unsuccessful — no products have been identified [98,100]. In only one case, in the acylation of the sodium salt of nitroethane, Nef [94] and then Jones [95] succeeded in isolating ethoxycarbonylacetohydroxamic (XXXI) and ethoxycarbonylethylnitrolic (XXXII) acids:



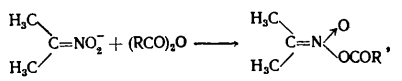
(XXXI) (XXXII)

Several papers describe the acylation of mononitro-compounds by acid anhydrides. On heating mononitroalkanes (nitromethane, nitroethane, 1-nitropropane, and phenylnitromethane) with acetic anhydride in the presence of sodium acetate or pyridine, Urbański [108] obtained in all cases only triacetylhydroxylamine (XXXIII). He believes that initially the nitro-compounds isomerise to the *aci*-form (XXXIVa) or nitrosohydroxy-compounds (XXXIVb) and then to hydroxamic acids (XXXV); the latter then undergo cleavage and acetolysis with formation of compound (XXXIII) and carboxylic acids:



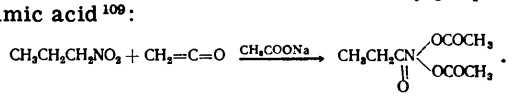
(XXXIVa) (XXXIVb) (XXXV) (XXXIII)

Quite different results were obtained in the reaction of acid anhydrides with secondary nitroalkanes. Thus acetic and propionic anhydrides react with 2-nitropropane (in toluene in the presence of potassium acetate) or its sodium salt (in ethereal suspension) to give relatively stable nitronic anhydrides [105] †:

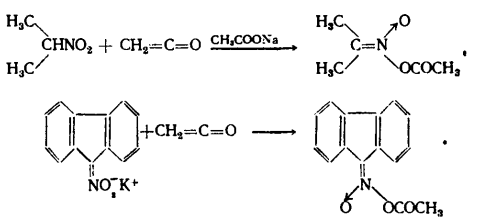


where R = CH_3 and C_2H_5. Unlike acetic or propionic anhydride, benzoic anhydride is completely inert under analogous conditions [105].

When keten is used as the acylating agent, the nature of the reaction products also depends on whether the initial nitro-compound is primary or secondary. Thus 1-nitropropane reacts with keten to form *NN*-diacetylpropiohydroxamic acid [109]:



Phenylnitromethane behaves similarly, its sole reaction product being acetylbenzohydroxamic acid [83]. In contrast to the primary nitro-compounds, the secondary compounds yield nitronic anhydrides on reacting with keten [83,109]:



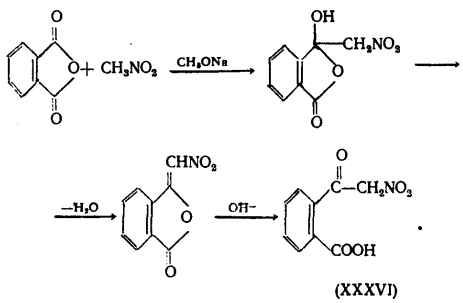
Thus in all the cases enumerated above O-acylation occurred. Only a few examples of acylation at the carbon atom with formation of α-nitroketones are described in the literature. In the study of the reaction of nitromethane with phthalic anhydride in the presence of sodium methoxide, Gabriel [110] obtained a very low yield of 2-nitroacetylbenzoic acid (XXXVI). He believes that the first stage of the process involves the addition of nitromethane

§ In another study it was shown that, in the reaction between the sodium salt of 2-nitropropane and benzoyl chloride in ether (in the form of suspension), only benzoic acid is formed even under anhydrous conditions [105].

¶ White and Considine [104] showed that, contrary to the data of Wislicenus and Pfeilsticker [106], the formation of the C-acylation product, 1-benzoyl-3-nitroindene, in the reaction of the potassium salt of 3-nitroindene with benzoyl chloride is also unlikely.

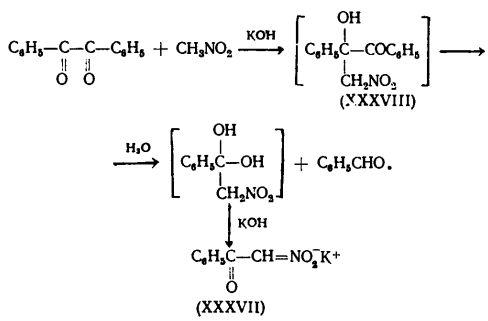
† This was subsequently confirmed by Urbański and Gurzyńska [109].

to the carbonyl double bond of the anhydride with subsequent elimination of a water molecule and hydrolysis:



(XXXVI)

In another study Yakubovich [111] treated nitromethane with benzil in the presence of twice the required amount of potassium hydroxide and obtained the potassium salt of ω-nitroacetophenone (XXXVII) and a whole series of other products. In his view, initially nitromethane adds to one of the carbonyls and then the addition product (XXXVIII) is cleaved to (XXXVII):



(XXXVII)

Nevertheless, it proved impossible to isolate compound (XXXVIII) as an intermediate; on the other hand, in the reaction between nitromethane and diacetyl an addition product of this type is formed smoothly.

In 1959 Bachman and Hokama [112,113] developed a general method for the synthesis of α-nitroketones by the *C*-acylation of primary nitroalkanes. They showed that *C*-acylation products will form only when rather unusual acylating agents, such as acyl cyanides, are employed:

$$RCH{=}NO_2^-M^+ + R'COCN \longrightarrow \underset{\displaystyle NO_2}{\overset{\displaystyle |}{R'COCHR}} + MCN,$$

where R = H, CH_3, and n-C_3H_7, R′ = CH_3 and C_6H_5, and M = Na and Li. The yields are 30–70%. When secondary nitroalkanes and used, α-nitroketones do not form. The lithium salts of nitroalkanes give better results than the sodium salts. t-Butyl alcohol, pyridine, and tetrahydrofuran are used as solvents. *O*-acylation products were never observed.

The authors offer the following explanation for this sharp difference in the behaviour (with respect to the salts of nitro-compounds) of acyl halides and acid anhydrides, on the one hand, and acyl cyanides, on the other. In the first case the reactions are so fast that thermodynamic equilibrium is not attained and *O*-acylation takes place, since the transition state then has a lower energy of formation than in *C*-acylation (by virtue of the higher electronegativity of oxygen compared with carbon). The reaction with acyl cyanides is much slower, equilibrium is attained, and the thermodynamic stability of the final products begins to play a decisive role; the latter is known to be always higher in the case of *C*-acyl derivatives [114].

III. ALKYLATION AND ACYLATION OF POLYNITRO--COMPOUNDS

In contrast to mononitro-compounds, whose alkylation has been the subject of a fairly large number of studies, the number of known examples of the alkylation of polynitro--compounds is much smaller. Thus in 1899 Hantzsch and Rinckenberger [115] obtained 1,1,1-trinitroethane by allowing the silver salt of nitroform to react with methyl iodide in ether:

$$C(NO_2)_3^-Ag^+ + CH_3I \longrightarrow CH_3C(NO_2)_3 + AgI.$$

The authors note that the potassium salt of nitroform does not enter into a similar reaction‡. They also state [115] that the reaction of the silver salt of nitroform with iodine cyanide gives trinitroacetonitrile:

$$C(NO_2)_3^-Ag^+ + ICN \longrightarrow (NO_2)_3C{-}CN + AgI.$$

Somewhat later Hantzsch and Caldwell [117] established that, when the silver salt of nitroform is allowed to react with methyl iodide at -75°, the initial step is the formation of the addition product $C(NO_2)_3Ag.2CH_3I$, which on raising the temperature is converted into trinitroethane in non--polar solvents. In the presence of hydroxyl-containing solvents (for example alcohols) this complex yields only the free nitroform. On the other hand, the reaction of the silver salt of nitroform with methyl iodide in aqueous, alcoholic, or ethereal solution gives only trinitroethane and traces of nitroform. The authors explain these results by postulating that in solution the silver salt reacts in the ionic form yielding the more stable *C*-alkylation product (trinitroethane); on the other hand, its addition product with methyl iodide reacts intramolecularly, forming the methyl ester $(NO_2)_2C{=}NO{-}OCH_3$. The latter, being unstable in a non-polar medium, isomerises to trinitroethane and in the presence of water hydrolyses to nitroform [117,118].

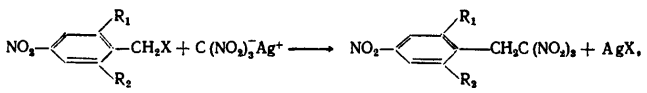
The same workers showed that the silver salt of nitroform reacts with ethyl iodide [117], benzyl iodide [115,117], allyl iodide [117], and bromoacetic ester [115], but no products were identified§. An attempt to make monochloromethyl ether [120] and triphenylchloromethane [17,120] react with the silver salt of nitroform was also unsuccessful, the reason being (according to the authors) that the water of crystallisation, which is always present in the molecule of the silver salt, hydrolyses the above halogeno-derivatives faster than they can react.

Meisenheimer and Schwarz [120] and Hantzsch [121] showed that bromonitroform and iodonitroform do not react with the silver salt of nitroform. In 1947 a paper was published, describing the alkylation of the silver salt of nitroform with various substituted benzyl halides [122] [*p*-nitrobenzyl bromide, 2,4,6-trinitrobenzyl iodide, *p*-di(iodomethyl)benzene, 1,3-di(iodomethyl)-5-nitrobenzene, and

‡ According to a recent communication [116], on carrying out the reaction in acetone, it proved possible to obtain 1,1,1-trinitroethane from the potassium salt of nitroform and methyl iodide (yield not indicated).

§ According to patent data [119], 4,4,4-trinitrobut-1-ene forms on reaction between the silver salt of nitroform and allyl bromide (in ether).

1,3,5-tri(iodomethyl)benzene], the products being the corresponding trinitroethyl derivatives of benzene, for example



where R_1 and R_2 = H and NO_2 and X = Br and I. The reactions were carried out in ether. The authors noted that in all cases they also observed the formation of unstable coloured oils (probably *O*-alkylation products), which decomposed with evolution of nitrogen oxides.

In 1952 an American patent [123] described the preparation of 1,1,1,2- and 1,1,1,3-tetranitropropane by the reaction of the silver salt of nitroform (in boiling ether) with the corresponding halogenonitro-compounds — 1-bromo-1-nitro- and 1-bromo-2-nitro-ethane. However, the patent gives no experimental details and the yields of the products are not stated.

In 1963 Hammond et al. [124] described the alkylation of the silver salt of nitroform with various halogeno-derivatives. The reaction in acetonitrile solution was studied in greatest detail. The authors showed that primary straight-chain alkyl iodides and also allyl bromide and iodide give the corresponding *C*-alkylation products in yields of 30–60%:

$$C(NO_2)_3^-Ag^+ + RX \xrightarrow{CH_3CN} RC(NO_2)_3 + AgX,$$

where R = n-alkyl and $CH_2{=}CHCH_2$ and X = I and Br. Secondary and cyclic alkyl halides and propargyl bromide, 1,3-di-iodopropane, and 1,4-dibromobutyne yield a complex mixture of products which could not be identified¶; allyl chloride, 1-bromo-2,4-dinitrobenzene, and 1-iodo-2-nitrobenzene do not react at all. When α-halogeno-acids are used, the corresponding nitrates are formed instead of the expected products, as a result of the substitution of the halogen by the nitrate group. The authors explain the failure of the above syntheses by the *O*-alkylation of the silver salt of nitroform under these conditions with formation of unstable nitronic esters:

The latter decompose with liberation of nitrate ions. The authors believe that another possible pathway involving the formation of nitrates, the gradual decomposition of the silver salt of nitroform to yield nitrate ions, is unlikely.

They also showed [124] that in the reaction of the silver salt of nitroform with chloromethyl ether and bromomethyl acetate the only product is trinitroethanol whose formation can be explained by the condensation of nitroform with formaldehyde, produced by the decomposition of the initial α-halogeno-ethers. The reaction of t-butyl bromide gave only *N*-t-butylacetamide — the product of the reaction of the halide with the solvent (acetonitrile). Hammond et al. [124] showed that the use of other solvents in the alkylation of the silver salt of nitroform (methyl and ethyl acetate, methyl and ethyl formate, acetone, ethanol, benzene) does not increase the yield compared with that obtained in acetonitrile, but the reactions are much faster. In contrast to the system in acetonitrile, in methyl acetate they were able to achieve the reaction of the silver salt with epi-iodohydrin and β-methylallyl bromide, the products, 4,4,4-trinitro-1,2-epoxybutane and 2-methyl-4,4,4-trinitrobut-1-ene, being obtained in yields of 19 and 27% respectively [124].

The study of the kinetics of the reaction of the silver salt of nitroform with methyl iodide in acetonitrile at 25.5° showed that the reaction is of third order overall, i.e. the silver cation participates as an electrophilic catalyst forming an ion pair in the transition state [124]:

$$C(NO_2)_3^- + R{-}I + Ag^+ \rightarrow (NO_2)_3C^-R^+IAg.$$

Thus the reaction is simultaneously of both S_N1- and S_N2-type.

Recently Tartakovskii et al. [126] showed that, when nitroform is treated with diazomethane, *O*-alkylation occurs with the formation of an unstable, very reactive nitronic ester.

Only a few papers have been published on the alkylation of salts of 1,1-dinitroalkanes (mainly silver salts). Duden [127] showed in 1893 that the silver salt of dinitromethane reacts with methyl iodide and ethyl iodide (in the absence of solvent) with the formation of the expected 1,1-dinitroalkanes:

$$HC(NO_2)_2^-Ag^+ + RI \rightarrow RCH(NO_2)_2 + AgI,$$

where R = CH_3 and C_2H_5. The author notes that the reactions are far from smooth, the products containing a considerable amount of unstable oils, which decompose even on slight heating.

In 1894 Nef [100] found that, when the silver salt of 1,1-dinitroethane reacts with methyl and ethyl iodide, the expected 2,2-dinitropropane formed only in the first case and even then in a low yield. The main products of the reaction were ethylnitrolic acid and the corresponding aldehyde (formaldehyde or acetaldehyde) and also free 1,1-dinitroethane. The author explains the formation of these products by the preferential *O*-alkylation of the silver salt of dinitroethane, resulting in the nitronic ester (XXXIX) which is unstable to heat and decomposes to ethylnitrolic acid (XL) and an aldehyde:

where R = H and CH_3.

A quite recent publication described the phenylation, at the carbon atom, of the potassium salts of 1,1-dinitroethane and 1,1-dinitropropane with diphenyliodonium toluenesulphonate [91]:

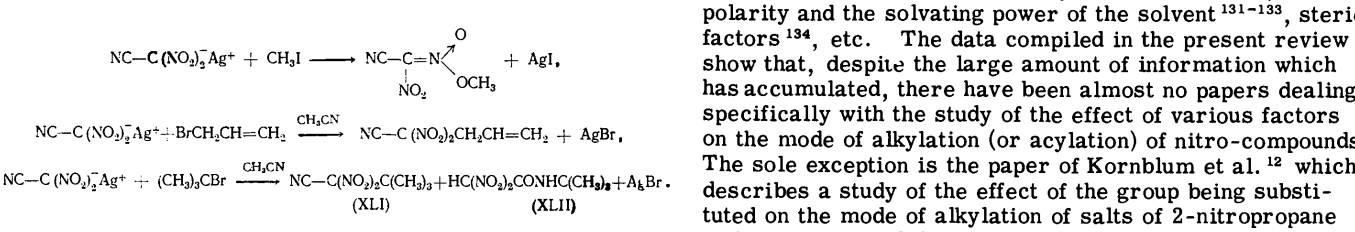
$$RCH_2C(NO_2)_2^-K^+ + (C_6H_5)_2I^+Tos^- \xrightarrow{t\text{-}C_4H_9OH} RCH_2C(NO_2)_2C_6H_5 + C_6H_5I + KTos,$$

where R = H and CH_3. The reaction is carried out in boiling t-butyl alcohol, the yields of 1-phenyl-1,1-dinitroalkanes being 67–68%. The authors note that, when dimethylformamide is used as the reaction medium, the desired products are formed in yields less than 5%, the principal product being nitrobenzene. The attempt to use the potassium salt of phenyldinitromethane in a similar reaction was unsuccessful.

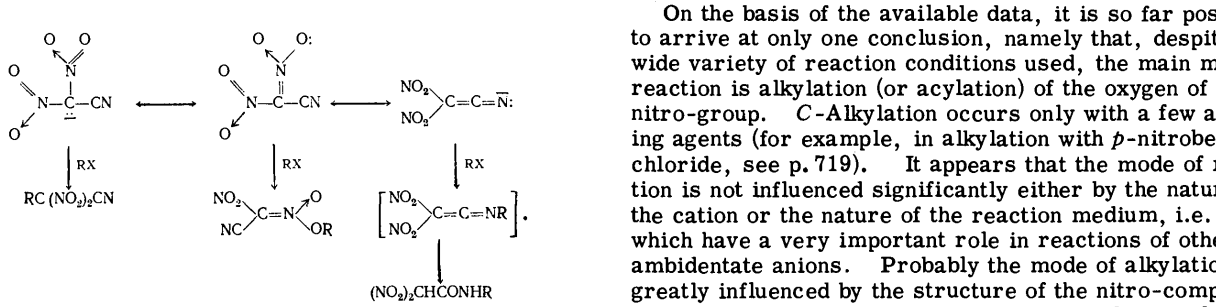
Unusual results were obtained in the alkylation of the silver salt of dinitroacetonitrile [124,128]. As a rule no identifiable products can be obtained in reactions of this kind. Only with methyl iodide, t-butyl bromide, and allyl bromide is the reaction relatively successful; with methyl iodide, only *O*-alkylation takes place (a stable methyl ether forms in 58% yield), the reaction with allyl bromide gives the *C*-alkylation product (yield 35%), while in the reaction

¶ According to patent data [125], 1,1,1,6,6,6-hexanitrohex-3-yne can be obtained by the reaction of the silver salt of nitroform with 1,4-dibromobut-2-yne in methyl acetate.

with t-butyl bromide a mixture of *C*- and *N*-alkylation products is formed [compounds (XLI) and (XLII) respectively, in yields of 17 and 18%]:



The authors' explanation of the results is that, being "polydentate" (i.e. having several reaction centres), the anion of dinitroacetonitrile can be alkylated in one of three ways, yielding *C*-, *O*-, or *N*-alkyl derivatives:



These results clearly contradict the generally accepted theory of Kornblum et al.[129] according to which the closer is the transition state in nucleophilic substitution reactions to a carbonium ion, the greater the probability of the formation of a bond with the most electronegative atom of the polydentate anion (in the anion of dinitroacetonitrile such atoms are the oxygen of the nitro-group and the nitrogen of the cyano-group). Allyl bromide and t-butyl bromide are known to form carbonium ions much more readily than methyl iodide (the fact that t-butyl bromide reacts with the silver salt of dinitroacetonitrile as a carbonium ion is demonstrated by the formation of the same products in the analogous reaction of t-butyl alcohol[128]). Nevertheless, *C*-alkylation takes place with allyl and t-butyl bromides. The authors explain this as follows: the transition state in these reactions, involving the participation of large planar ions, is sterically facilitated and therefore when two ions approach one another there is a greater probability of the formation of a bond with the geometric centre of the charge density of the dinitroacetonitrile anion (i.e. with the carbon atom) than with an individual electronegative atom (oxygen or nitrogen)[124,128].

There are no publications dealing with the acylation of polynitro-compounds, only isolated, negative data being available. Thus Hantzsch and Rinckenberger[115] noted that it is impossible to achieve the reaction of the silver salt of nitroform with chlorocarbonic ester. The use of acyl halides as acylating agents in reactions with the silver salt of nitroform (in acetonitrile) only results in the formation of the corresponding carboxylic acids[124].

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The data presented in this review show that alkylation and acylation reactions are typical and perhaps the most distinctive examples of the dual reactivity of nitro-compounds. The mode of alkylation (or acylation) of ambidentate anions (i.e. anions with two reaction centres), to which the anions of nitro-compounds belong, is known to be influenced by a number of factors: the nature of the cation[129], the heterogeneity or homogeneity of the medium[130], the polarity and the solvating power of the solvent[131-133], steric factors[134], etc. The data compiled in the present review show that, despite the large amount of information which has accumulated, there have been almost no papers dealing specifically with the study of the effect of various factors on the mode of alkylation (or acylation) of nitro-compounds. The sole exception is the paper of Kornblum et al.[12] which describes a study of the effect of the group being substituted on the mode of alkylation of salts of 2-nitropropane with *p*-nitrobenzyl derivatives. For this reason, systematic studies in this field are necessary to elucidate the influence of the structure and reaction conditions on the mode of alkylation of nitro-compounds.

On the basis of the available data, it is so far possible to arrive at only one conclusion, namely that, despite the wide variety of reaction conditions used, the main mode of reaction is alkylation (or acylation) of the oxygen of the nitro-group. *C*-Alkylation occurs only with a few alkylating agents (for example, in alkylation with *p*-nitrobenzyl chloride, see p. 719). It appears that the mode of reaction is not influenced significantly either by the nature of the cation or the nature of the reaction medium, i.e. factors which have a very important role in reactions of other ambidentate anions. Probably the mode of alkylation is greatly influenced by the structure of the nitro-compound itself. Thus salts of phenylnitroacetonitrile are always acylated at the oxygen only, even with *p*-nitrobenzyl chloride[4], which as a rule alkylates mononitro-compounds at the carbon atom.

After the manuscript had been sent to the editors, a number of papers with a direct bearing on the present topic have been published and we decided it was necessary to consider them if only briefly.

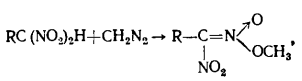
1. Mononitro-compounds. The work of Teuber and Glosauer[135], who succeeded in obtaining the corresponding *C*-alkylation products by treating the sodium salts of 2-nitropropane and nitrocyclohexane with *o*-nitrobenzyl chloride, is noteworthy. There has also been an interesting communication[136] according to which the reaction of triphenylchloromethane with the sodium salt of nitrocamphor gives a stable nitronic ester (in 44% yield) — an *O*-alkylation product. In another study[137] the intermediate stages of the reaction of triphenylchloromethane with the silver salt of phenylnitroacetonitrile were investigated (c.f. Ref. 19).

Polyanskaya et al.[138] state that in the reaction of nitroacetic ester with alkyl halides in the presence of amines (for example triethylamine), esters of α-nitroalkanecarboxylic acids are formed, i.e. alkylation at the carbon atom takes place. A few more examples of *C*-alkylation of 2-nitropropane (in the form of the sodium salt) with β-chlorovinyl ketones have been described by Belyaev and Shamanovskaya[139].

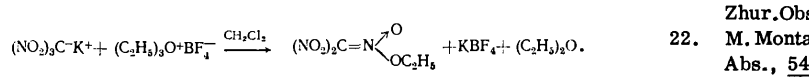
Two papers describe interesting cases of intramolecular *C*-alkylation of mononitro-compounds. Thus on treatment of 1-iodo-3-nitropropane with lithium amide in liquid ammonia, nitrocyclopropane forms in high yield (87%).[140] Etheredge[141] found that a bridge nitro-compound, 1-nitrobicyclo[3,2,1]octane, forms in 19% yield in the reaction of 2-(3-nitrocyclohexyl)ethyl toluenesulphonate with sodium hydride in dimethylformamide.

2. Polynitro-compounds. Here mention must be made in the first place of the work of Tartakovskii and

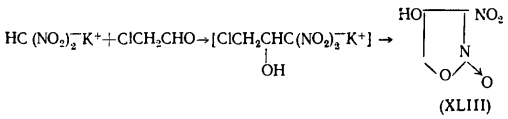
coworkers on the preparation of *O*-methyl derivatives of dinitromethane [142] and nitroform [143] (see also Ref. 126) by the action of diazomethane in benzene on dinitromethane and nitroform respectively:



where R = H and NO_2. The same workers obtained [143] the *O*-ethyl derivative of nitroform by alkylating the potassium salt of nitroform with triethyloxonium fluoroborate:

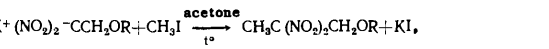


In another paper [144] they describe the synthesis of a cyclic nitronic ester (XLIII) by the intramolecular *O*-alkylation of the potassium salt of 1-chloro-3,3-dinitro-2-propanol — an intermediate in the reaction between the potassium salt of dinitromethane and chloroacetaldehyde:



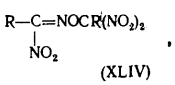
(XLIII)

Recently Ungnade and Kissinger [145] described two examples of *C*-alkylation (in yields of 80–90%) of salts of 2,2-dinitroethyl alkyl ethers with methyl iodide:



where R = CH_3 and $ClCH_2CH$.

Ustynyuk et al.[146] studied the action of various acylating agents (acid chlorides and anhydrides and acetyl nitrate) on salts of 1,1-dinitroethane and 1,1-dinitropropane and established that in all cases the reactions result in the formation of self-condensation products of the initial dinitroalkanes (XLIV) (in yields of 30–50%):



(XLIV)

where R = CH_3 and C_2H_5. The structure of compound (XLIV) was confirmed by spectroscopic methods [147].

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OLEFIN SYNTHESIS WITH P(O)-ACTIVATED REAGENTS

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I. INTRODUCTION

When arylphosphoranes of the type $(Ar)_3P=CR'R''$ are allowed to act upon carbonyl compounds in the well-known Wittig reaction[1-4], various olefins with double bonds in specified positions may be obtained. This reaction has found wide application in practical organic synthesis. However, it has important limitations. Aldehydes with strongly electron-donor substituents near the reaction centre do not enter into this reaction[5]; phosphoranes containing electron-acceptor groups, for example CN, $COOC_2H_5$, etc., do not as a rule react with ketones under the usual conditions[6,7]. Attempts have been made to overcome these difficulties, for example by heating the components for many hours at 100–170° in sealed tubes[8], by carrying out the reaction in high-boiling solvents, etc.[9,10] However, severe reaction conditions of this kind have an unfavourable effect on the yields of unsaturated compounds and in many cases are altogether inadmissible. It has recently been observed[11,12] that benzoic acid catalyses the reaction of ethoxycarbonylethylenetriphenylphosphorane with ketones, but the region of applicability of this catalytic effect has not yet been determined.

However, perhaps the most important disadvantage of the Wittig reaction consists in the difficulty of isolating in the majority of cases the unsaturated product. In this connection development and modification of the Wittig reaction is of considerable interest.

In 1958 Horner and coworkers[13-20] discovered the P(O)-activated olefin synthesis in which olefins and their derivatives with various functional groups are obtained by the reaction of aldehydes and ketones with organophosphorus compounds containing the $P(O)-CH_2$ group. Phosphonate salts, phosphonate esters, and phosphine oxides have been suggested as P(O)-activated reagents for olefin synthesis. The formation of unsaturated compounds by P(O)-activated synthesis can be represented by the reaction

$$R'-CO-R''+R_2P(O)-CH_2-R'''\rightarrow R'R''C=CHR'''+R_2P(O)OH.$$

The use of P(O)-activated reagents for olefin synthesis has a number of advantages over the Wittig reaction. Such reagents are more reactive with respect to carbonyl compounds, in particular ketones, since they are more nucleophilic than phosphoranes. In a special study Horner and coworkers[21] compared olefin synthesis using P(O)-activated reagents with olefin synthesis using phosphoranes in the Wittig reaction, and showed that, in the presence of the competing reactions of $(C_6H_5)_3P=CH-C_6H_5$ and $(C_6H_5)_2P(O)-CH_2-C_6H_5$ with carbonyl compounds in proportions of 1:1:1, the olefin $C_6H_5-CH=CRR'$ forms preferentially from benzyldiphenylphosphine oxide. The isolation of olefins in P(O)-activated synthesis is much simpler, since the unsaturated compounds produced can be readily separated from the highly water-soluble alkali metal salts of alkylphosphoric acids, while in the Wittig reactions special procedures must be used to separate the olefin from triphenylphosphine oxide. Finally, compared with the Wittig reagents (phosphoranes), the reagents for P(O)-activated olefin synthesis are more readily accessible, since they can be obtained relatively simply by the well-known reactions of Arbuzov, Michaelis–Becker, and others.

Like the Wittig reactions, P(O)-activated olefin synthesis makes it possible to increase the length of the carbon chain and introduce C=C bonds in specified positions. The yields of the unsaturated compounds are usually much higher than in the Wittig reaction.

The present article reviews the publications concerned with P(O)-activated olefin synthesis.

II. REAGENTS FOR P(O)-ACTIVATED OLEFIN SYNTHESIS

The methods for the preparation of organophosphorus compounds containing the $P(O)-CH_2$ group, which is essential for P(O)-activated olefin synthesis, have been thoroughly developed and the chemical properties of these compounds have been investigated fairly completely. There exist many reviews and monographs on this problem (see, for example, Refs. 22–33).

The reagents usually employed for P(O)-activated olefin synthesis are esters (most often ethyl) of phosphonic acids $(RO)_2P(O)-CH_2-R'$ (R' may be an aliphatic or an aromatic radical or any functional group) and esters of β-oxophosphonic acids $(RO)_2P(O)-CH_2-CO-R'$ (R' is an alkyl or aryl residue). In many cases alkyldiphenylphosphine oxides, and in particular benzyldiphenylphosphine oxide, proved to be satisfactory reagents for this synthesis[34]. Phosphonoacetic ester, first obtained by Arbuzov and Dunin[35] in 1914, is very often used in P(O)-activated olefin synthesis; the method of synthesis of this ester was improved in subsequent work[36-40]. To introduce two ethylene bonds, reagents for P(O)-activated diolefin synthesis, containing two P(O) groups, are used. The substances which have become important for these purposes are the tetraethyl esters of bisphosphonic acids, $(C_2H_5O)_2P(O)-(CH_2)_n-P(O)(OC_2H_5)_2$ (n = 1–8) and $(C_2H_5O)_2P(O)-CH_2-X-CH_2-P(O)(OC_2H_5)_2$ (X is one or several vinylene groups or benzene rings), and also the very readily available so-called "dioxide" $(C_6H_5)_2P(O)-CH_2-P(O)(C_6H_5)_2$.[41,42]

The most important method for synthesising phosphonic esters is the Arbuzov reaction[43-46], discovered in 1905, which is known as the "Arbuzov rearrangement":

$$(RO)_3P+R'—Hal \rightarrow (RO)_2P(O)—R'+R—Hal \quad (Hal=Cl, Br, I).$$

The possibilities of the Arbuzov reaction have been by no means exhausted. New papers continue to appear in which organophosphorus compounds suitable for P(O)-activated olefin synthesis are described[47,48]. It should be noted that the limitations which may arise when the Arbuzov reaction is applied to α-halogeno-carbonyl compounds in connection with the so-called Perkow reaction or rearrangement[49-59] (see Lichtentahler's review[60]) are unimportant in the preparation of valuable reagents for P(O)-activated olefin synthesis in which the methylene group is between the P(O) and carbonyl groups. In 1965 Arbuzov and coworkers[61] established that the reactions of diphenylphosphinous acid with chloroacetone yield mixtures containing predominantly β-oxophosphonic esters together with unsaturated phosphate esters. On the other hand with ω-bromoacetophenone, the Arbuzov reaction takes place almost exclusively with good yields of diphenylphenylacylphosphine oxide which is a valuable reagent for P(O)-activated olefin synthesis. According to the communication of Imaev and coworkers[62], dialkylphosphonoacetophenones having the general formula $(RO)_2P(O)-CH_2-CO-C_6H_5$ (R = CH_3 and $n-C_3H_7-C_8H_{17}$) can be obtained, in high yield, by the Arbuzov reaction from ω-bromoacetophenone and a number of phosphite tri-esters (except the ethyl ester). Since the reaction of α-halogeno-aldehydes with trialkyl phosphites gives virtually no normal products of the Arbuzov reaction[60], Razumov and Moskva[63] used the acetal of bromoacetaldehyde to prepare phosphonoacetaldehyde in 70% yield:

$$CH_2Br—CH(OC_2H_5)_2+(C_2H_5O)_3P \rightarrow C_2H_5Br+$$

$$+(C_2H_5O)_2P(O)—CH_2—CH(OC_2H_5)_2 \xrightarrow[HCl]{H_2O} 2C_2H_5OH+(C_2H_5O)_2P(O)—CH_2—CHO.$$

The Michaelis–Becker reaction[64] is of practical importance for the synthesis of reagents for P(O)-activated olefin synthesis; it is based on the reaction of alkali metal salts of phosphite di-esters with organic compounds containing reactive halogen atoms:

$$(RO)_2P(O)Na+R'—Hal \rightarrow (RO)_2P(O)—R'+NaHal \quad (Hal=Cl, Br, I).$$

The applicability of the Michaelis–Becker method is somewhat reduced as a result of a number of side-reactions. In particular the reaction with α-halogeno-carbonyl compounds is as a rule anomalous, since esters of epoxyphosphonic acid are formed preferentially[65,66]. The method developed by Normant and coworkers[67] for the preparation of phosphonates containing a carbonyl group, by the reaction of sodium diethyl phosphite with ethers derived from the enols of α-halogeno-carbonyl compounds, is of interest in this connection. The ethers are readily obtained by the pyrolysis of α-halogeno-diacetals. The resulting normal products of the Michaelis–Becker reaction are converted after hydrolysis into β-diethylphosphonocarbonyl compounds:

$$R—CH_2—C(OR')_2—CH_2—X \rightarrow R'—OH+R—CH=C(OR')—CH_2—X \rightarrow$$
$$\xrightarrow[NaX]{+(C_2H_5O)_2P(O)Na} R—CH=C(OR')—CH_2—P(O)(OC_2H_5)_2 \rightarrow$$
$$\xrightarrow[-R'—OH]{+H_2O} (C_2H_5O)_2P(O)—CH_2—CO—CH_2—R.$$

A number of β-oxophosphonic esters have been prepared by this method[68].

The third fundamentally important method for the preparation of organophosphorus compounds of various complexity containing $P(O)-CH_2$ groups consists in the addition of dialkylphosphorous acids and acid esters of alkyl- and aryl-phosphonous acids to ethylenic hydrocarbons and their various derivatives. This method has been proposed and largely developed by Pudovik and coworkers; data concerning the preparation of many compounds suitable for P(O)-activated olefin synthesis are presented in Pudovik's review[26]. Subsequently a number of papers were published with data on the synthesis of organophosphorus compounds of this kind using unsaturated compounds[69-75].

The hydrogen atoms in the methylene group of organophosphorous compounds containing the $P(O)-CH_2$ unit are reactive. This reactivity is due to the effect of the adjacent P(O) group involving the semipolar phosphorus–oxygen bond[76-79], with the negative charge located on the oxygen atom, i.e. $\rangle P=O \leftrightarrow P^+-O^-$. Since 1929 Arbuzov showed[80,81] that the hydrogen atoms of the methylene group in phosphonoacetic and alkylphosphonic esters, etc. are similar to those in acetoacetic ester, being readily replaced by alkali metals. In some cases the hydrogen atoms of the methylene group are so reactive that on reacting with a Grignard reagent they cause the evolution of the hydrocarbon and form an organophosphorus–magnesium compound[82]; the reaction with phenyl-lithium is similar[13] and in the Chugaev–Tserevitinov [Zerevitinov] reaction the evolution of active hydrogen reaches quantitative yields[15]. The mobility of the hydrogen atoms of the methylene group is also revealed in Claisen condensation with carboxylic acid esters[15,83,84], in condensation of the crotonic acid type with aldehydes[42,85,86], and in addition reactions to double carbon–carbon bonds in electrophilic unsaturated compounds[26].

III. MECHANISM OF P(O)-ACTIVATED OLEFIN SYNTHESIS

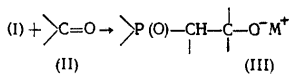
In practice the P(O)-activated olefin synthesis is carried out under mild conditions, often with slight and brief heating of the initial reactants in a suitable solvent (dimethylformamide, 1,2-dimethoxyethylene, cyclohexane, benzene, toluene). It has been found that in ether and anisole the olefin yields are low, while in chlorobenzene the reaction virtually does not occur at all[20]. Usually the condensing reagent and then the carbonyl component are added to a solution of a P(O)-activated reagent for olefin synthesis. At the end of the reaction the mixture is treated with water which dissolves the phosphonate salts, the olefins being isolated from the organic layer.

In a special investigation devoted to the study of the mechanism of the P(O)-activated olefin synthesis, Horner and coworkers[20] concluded that the reaction involves three stages, from each of which it is possible to isolate and characterise the intermediate products in some cases. In the first stage the reactive hydrogen atom of the methylene group of the P(O)-activated reagent is replaced by a metal to give a *C*-metallated compound (I):

$$\rangle P(O)—\underset{|}{CH_2}+M^+ \rightarrow \rangle P(O)—\underset{|}{\bar{C}H}M^+ + {}^1/_2H_2 \quad (M=Li, Na, K).$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (I)$$

When alkali metal hydrides, amides, or alkoxides and metal alkyls or metal aryls are used as metallating agents, hydrogen, ammonia, alcohols, or hydrocarbons are evolved respectively. In the second stage compound (I), which behaves as a usual organometallic compound, reacts with the

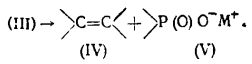
carbonyl compound (II) to form a β-hydroxy-derivative (III) of the P(O)-compound:



(II) (III)

Cases of this type of condensation in which compounds of type (III) were isolated, have been described[87-93].

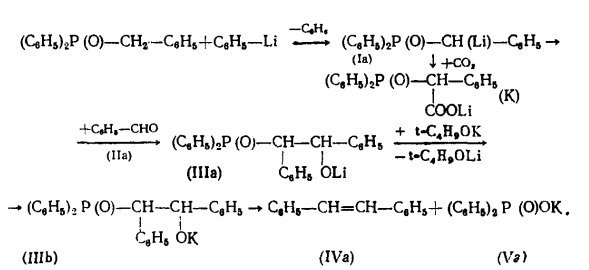
In the third stage compound (III) decomposes into an olefin (IV) and a phosphorus-containing acid anion (V):



(IV) (V)

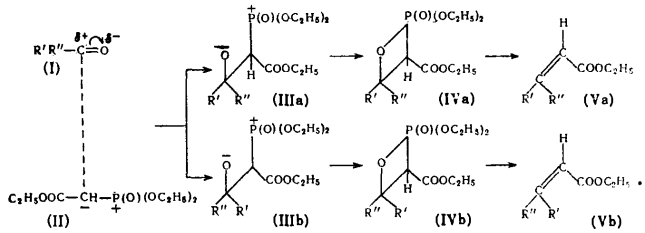
The third stage is due to the characteristic high affinity of phosphorus for organic oxygen (carbonyl oxygen)[94,95]. On the basis of the available data concerning the mechanism of the Wittig reaction between alkylidenephosphoranes and carbonyl compounds[2,3], the similarity of this reaction to P(O)-activated olefin synthesis, and the similarity of the electronic structures of P(O)-activated reagents for such synthesis, Wadsworth and Emmons[96] proposed a mechanism for P(O)-activated olefin synthesis similar to that described above.

The stages of the P(O)-activated olefin synthesis described above are to some extent hypothetical, since in most cases the intermediate compounds (I) and (III) cannot be isolated or identified. The stability of the metallated compound (I) and the hydroxy-derivative (II) of the P(O)-compound has been found to depend significantly on the nature of the alkali metal. When lithium metallating agents are used, compound (I) can be identified and compound (III) can be isolated[15,19]. Using the synthesis of stilbene as an example, Horner and coworkers[15] showed that stilbene forms in the reaction between benzyldiphenylphosphine oxide and benzaldehyde in the presence of lithium-, sodium-, and potassium-containing condensing agents. When sodium or potassium derivatives are used, the intermediates (I) and (III) cannot be detected. However, in the presence of phenyl-lithium the *C*-lithium compound (Ia) formed in the first stage was identified by its reaction with carbonic acid which yields a carboxylic acid (K). In the second stage of the reaction [after the addition of benzaldehyde to a solution of compound (Ia)] the β-hydroxy derivative (IIIa) of the P(O)-compound was isolated; on heating in toluene with potassium t-butoxide, it was converted into stilbene (IVa) and a salt of diphenylphosphinic acid (Va). It is assumed that the lithium compound (IIIa) is initially converted into an unstable potassium derivative (IIIb) which then decomposes into substances (IVa) and (Va). This can be represented as follows:



(IIIb) (IVa) (Va)

Yanovskaya and Kucherov[9] studied the stereochemistry of P(O)-activated olefin synthesis and established, on the basis of numerous experimental data, that the reaction of, for example, aldehydes with diethyl ethoxycarbonylmethylphosphonate is stereospecific and yields only the *trans*-isomers. Later these workers showed that sterically hindered ketones virtually do not enter into this reaction. Sterically unhindered ketones form with P(O)-activated reagents for olefin synthesis mixtures of *cis*- and *trans*-isomers. The absence of stereospecificity is the principal difference between the behaviour of aldehydes and ketones in this reaction. This can be explained in terms of the latest data on the mechanism of the Wittig reaction[97-100] and Yanovskaya and Kucherov's interpretation[9] of the stereospecificity of the formation of unsaturated compounds from phosphoranes and aldehydes and ketones. In P(O)-activated olefin synthesis, the formation of geometrical isomers can be represented by the scheme given below. As in the Wittig reaction, the nucleophilic attack by the carbon atom of the P(O)-activated reagent (II) for olefin synthesis on the carbon atom of the carbonyl compound (I) can result in the formation of *cis*- and *trans*-betaines (IIIa) and (IIIb) which lead to *cis*- and *trans*-olefins (Va) and (Vb) via the cyclic transition states (IVa) and (IVb):



(I) (II) (IIIa) (IIIb) (IVa) (IVb) (Va) (Vb)

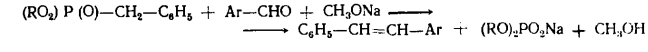
In conformity with Cramm's rule[101], with aldehydes (R′ = H) the formation of the betaine (IIIb) occurs preferentially, which results in *trans*-olefins. With ketones having unbranched R′ and R″ radicals, the formation of (IIIa) and (IIIb) is equally likely, which implies an equal probability of the formation of the *cis*- and *trans*-isomers.

IV. SYNTHESIS OF OLEFINS

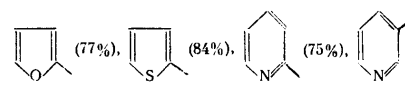
The main application of the method of P(O)-activated olefin synthesis has been to prepare olefins of various complexities with aromatic substituents and some of their heterocyclic analogues and also unsaturated acids and their derivatives.

1. Mono-Olefins and Their Hydrocarbon Derivatives

Stilbene and its analogues are obtained on condensation of carbonyl compounds with various condensing agents and P(O)-activated reagents for olefin synthesis. Stilbene, 2-stilbazole, 2-styrylfuran, and 2-styrylthiophen are obtained most simply on slight and brief heating of benzaldehyde or the corresponding heterocyclic aldehyde with diethyl benzylphosphonate in dimethylformamide in the presence of sodium methoxide[102]:



where Ar = C_6H_5 (yield 85%),



(here and below R = C_2H_5).

3-Stilbazole was obtained in the same way [15,20]. Stilbene can be synthesised in high yields also by the condensation of benzaldehyde with benzyldiphenylphosphine oxide [15,18], and if instead of benzaldehyde acetophenone is used, the product is α-methylstilbene [15]. By selecting suitable reactants with various substituents in the benzene rings, it is possible to obtain stilbenes with substituents in specified positions, for example [20]:

$$(RO)(C_6H_5)P(O)-CH_2-C_6H_4OCH_3\text{-}p + p\text{-}ClC_6H_4-CHO \longrightarrow (RO)(C_6H_5)P(O)OH + p\text{-}CH_3OC_6H_4-CH=CH-C_6H_4Cl\text{-}p.$$

Horne and coworkers [16,18] described two interesting methods for the preparation of stilbenes and their analogues by P(O)-activated olefin synthesis. In the first method triphenylphosphine oxide is heated in succession with sodium hydride and an aromatic aldehyde. This results in the formation of an olefin, benzene, and sodium diphenylphosphinate:

$$2(C_6H_5)_3P=O + 2NaH + 2Ar-CHO \longrightarrow Ar-CH=CH-Ar + 2(C_6H_5)_2PO_2Na + C_6H_6,$$

where Ar = C_6H_5, p-ClC_6H_4, α-$C_{10}H_7$, 9-$C_{14}H_{11}$ (from anthracene-9-aldehyde). If benzophenone is used instead of aldehydes, the product is tetraphenylethylene [17].

It was established that the olefin forms in stages. Initially when triphenylphosphine oxide is fused with sodium hydride (at about 200°), the products are benzene and sodium diphenylphosphine oxide (I), which then reacts with the added aldehyde, yielding the alkoxide of (α-hydroxybenzyl)diphenylphosphine oxide (II). The latter reacts with compound (I) and gives sodium diphenylphosphinate and a C-metallated derivative of benzyldiphenylphosphine oxide (III). Finally, compound (III) reacts with a second molecule of the aldehyde to form the olefin and a second molecule of sodium diphenylphosphinate. The reactions can be expressed as follows:

$$(C_6H_5)_3P=O + NaH \longrightarrow C_6H_6 + (C_6H_5)_2P(O)Na, \quad (I)$$
$$(I) + Ar-CHO \rightleftarrows (C_6H_5)_2P(O)CH(ONa)-Ar, \quad (II)$$
$$(I) + (II) \longrightarrow (C_6H_5)_2P(O)ONa + (C_6H_5)_2P(O)CH(Na)-Ar, \quad (III)$$
$$(III) + Ar-CHO \longrightarrow (C_6H_5)_2P(O)ONa + Ar-CH=CH-Ar.$$

In the second method stilbenes are obtained on auto-oxidation of derivatives of phosphine oxides or phosphonic esters. For example, benzyldiphenylphosphine oxide in benzene solution is mixed or shaken with potassium t-butoxide in an atmosphere of oxygen, the reaction mixture is then treated with water, and stilbene is isolated from the benzene layer. In general, stilbene synthesis can be represented thus:

$$2(C_6H_5)_2P(O)-CH_2-Ar + t\text{-}C_4H_9OK \xrightarrow{O_2} Ar-CH=CH-Ar + 2(C_6H_5)_2P(O)OK + t\text{-}C_4H_9OH,$$

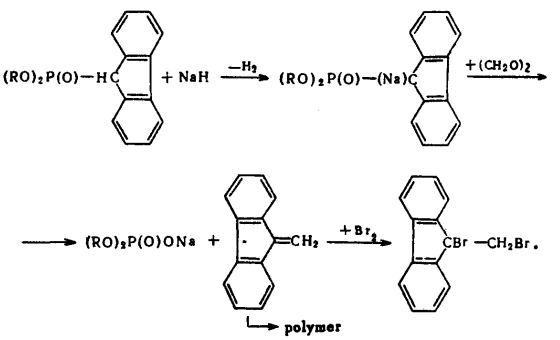
where Ar = C_6H_5, 3,4-$Cl_2C_6H_3$, and α-$C_{10}H_7$ (yield about 90%).

The study of this reaction showed [18] that the first stage involves the formation of a C-metallated phosphine oxide which is readily oxidised by molecular oxygen to a hydroxy-derivative, like the usual organometallic compounds. It is assumed that the oxidation goes via a stage in which a peroxy-compound is formed. As already mentioned, O-metallated oxides of α-hydroxyphosphines can break down reversibly into a phosphinic acid salt and a carbonyl compound [17], which immediately reacts with the C-metallated derivative of phosphine oxide to give the final reaction product — the olefin and the phosphinic acid salt. The various stages of the process can be represented in the following way:

$$(C_6H_5)_2P(O)-CH_2-Ar + t\text{-}C_4H_9OK \longrightarrow t\text{-}C_4H_9OH + (C_6H_5)P(O)CH(K)-Ar \xrightarrow{+O_2} (C_6H_5)_2P(O)-CH(O-OK)-Ar \xrightarrow{+(C_6H_5)_2P(O)CH(K)-Ar} 2(C_6H_5)_2P(O)-CH(OK)-Ar \rightleftarrows 2(C_6H_5)_2P(O)K + 2Ar-CHO,$$
$$(C_6H_5)_2P(O)-CH(K)-Ar + Ar-CHO \longrightarrow Ar-CH=CH-Ar + (C_6H_5)_2P(O)OK.$$

It has been found that, when lithium-containing metallating agents are used, it is possible to isolate O-lithium hydroxy-derivatives, which are stable unlike the O-sodium or O-potassium derivatives, since they have a lower affinity for carbonyl oxygen.

Apart from stilbenes, mono-olefins such as 1,1-diphenylethylene [13], 1-methyl-2,2-diphenylethylene [13,15], 2,2-diphenyl-1-n-propylethylene, 1-ethyl-1-methyl-2-phenylethylene [15], benzylidenecyclohexane [15,20], and triphenylethylene [13,15,18,29,96] have been obtained by the P(O)-activated synthesis. An interesting case of the P(O)-activated synthesis of mono-olefins is the reaction of diethyl fluorenylphosphonate with paraformaldehyde in the presence of sodium hydride [96]:



Since the resulting 9-methylenefluorene rapidly polymerises (particularly in the absence of solvent), the olefin formed is converted into the dibromo-derivative without being isolated first.

2. Diene and Polyene Hydrocarbons

P(O)-activated olefin synthesis has been successfully used to prepare unsaturated compounds containing two and more multiple carbon-carbon bonds. On combining together in the condensation process P(O)-activated reagents for mono- and di-olefin synthesis with mono- or di-carbonyl compounds, olefins with various degrees of unsaturation are obtained. Thus the reaction of diethyl benzylphosphonate with cinnamaldehyde yields 1,4-diphenylbuta-1,3-diene [20,96] and the reaction of benzyldiphenylphosphine with benzil gives 1,2,3,4-tetraphenylbuta-1,3-diene: [15]

$$(RO)_2P(O)-CH_2-C_6H_5 + C_6H_5-CH=CH-CHO \xrightarrow{t\text{-}C_4H_9OK} (RO)_2P(O)OK + C_6H_5-CH=CH-CH=CH-C_6H_5\ (80\%),$$
$$2(C_6H_5)_2P(O)-CH_2-C_6H_5 + C_6H_5-CO-CO-C_6H_5 \xrightarrow[(\text{or NaH})]{t\text{-}C_4H_9OK} 2(C_6H_5)_2P(O)OK + C_6H_5-CH=C(C_6H_5)-C(C_6H_5)=CH-C_6H_5\ (50\%).$$

Phenyl-substituted polyenes with a conjugated system of double bonds are formed when bis-P(O)-activated reagents for olefin synthesis and aliphatic-atomatic aldehydes or

ketones are used in the reaction. For example, 1,10-diphenyldeca-1,3,5,7,9-pentaene and 1,1,6,6-tetraphenylhexatriene are formed in the following process [20]:

$$(RO)_2P(O)-CH_2-CH=CH-CH_2-P(O)(OR)_2 + C_6H_5-CH=CH-CHO \longrightarrow$$
$$\xrightarrow{t\text{-}C_4H_9OK} C_6H_5-\overset{(A)}{(CH=CH)_3}-C_6H_5 + 2(RO)_2P(O)OK,$$
$$(A) + (C_6H_5)_2C=O \longrightarrow (C_6H_5)_2C=CH-CH=CH-CH=C(C_6H_5)_2 + 2(RO)_2P(O)OH.$$

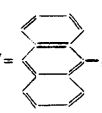
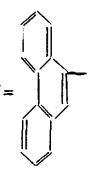
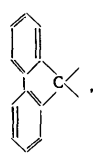
Aliphatic–aromatic dienes with methylene bridges which interrupt the conjugation chain are obtained when the oxides of n-alkylene-$\alpha\omega$-bisdiphenylphosphines are condensed with carbonyl compounds. For example [20]:

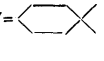
$$(C_6H_5)_2P(O)-(CH_2)_n-P(O)(C_6H_5)_2 + 2(C_6H_5)_2C=O \xrightarrow{t\text{-}C_4H_9OK}$$
$$\longrightarrow 2(C_6H_5)_2P(O)OK + (C_6H_5)_2C=CH-(CH_2)_{n-2}-CH=C(C_6H_5)_2 \quad (n=2, 4, 6).$$

The P(O)-activated synthesis has proved particularly valuable for the preparation of olefins such as distyryls [20], which are difficult to prepare otherwise and which have found application recently as light-protective media, as stabilisers for polymers and polyolefins, and as optical bleaching agents for high-molecular compounds. Thus the condensation of tetraethyl (*p*-phenylenedimethylene)-bisphosphonate (TEPP) with various aldehydes and ketones in dimethylformamide in the presence of sodium methoxide [103] or potassium t-butoxide [20] gives distyryls of various complexity in yields of 65–90%:

$$(RO)_2P(O)-CH_2-C_6H_4-CH_2-P(O)(OR)_2 + 2R'R''C=O \rightarrow$$
$$\rightarrow 2(RO)_2P(O)OH + R'R''C=HC-C_6H_4-CH=CR'R'',$$

where R′ = H and R″ = C_6H_5, R′ = H and R″ = *p*-$O_2NC_6H_4$, R′ = H and R″ = *p*-$(CH_3)_2NC_6H_4$, R′ = H and R″ = *p*-C_6H_5–C_6H_4,

R′ = H and R″ =  , R′ = H and R″ =  , R′ = R″ =  ,

R′ = H and R″ = α-$C_{10}H_7$, R′ = H and R″ = , R′ = R″ =  , and R′ = R″ = C_6H_5.

1,4-Distyryl is also obtained on condensing TEPP with terephthalic aldehyde, and the reaction of the same bis-P(O)-activated reagent for olefin synthesis with cinnamaldehyde gives an 84% yield of 1,4-di-(4-phenylbutadienyl)-benzene [20,96]. The same olefin is also the product of the condensation of cinnamaldehyde and (*p*-phenylenedimethylene)bis(diphenylphosphine oxide) [20]:

$$(RO)_2P(O)-CH_2-C_6H_4-CH_2-P(O)(OR)_2 + 2C_6H_5-CH=CH-CHO \rightarrow$$
$$\rightarrow 2(RO)_2P(O)OH + C_6H_5-(CH=CH)_2-C_6H_4-(CH=CH)_2-C_6H_5.$$

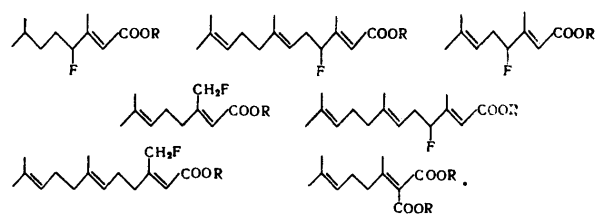
3. Synthesis of Aliphatic and Aliphatic-Aromatic Unsaturated Acids

P(O)-Activated olefin synthesis is a good method for preparing derivatives of unsaturated aliphatic and aliphatic-aromatic acids. This method has been used to synthesise quite a large number of esters and nitriles of $\alpha\beta$-unsaturated acids. The readily available (diethyl phosphono)acetic ester is usually employed as the P(O)-activated reagent for this type of olefin synthesis. The reaction is carried out in a suitable solvent (dimethylformamide, toluene, and others) in the presence of condensing agents (alkali metal alkoxides, metallic sodium, etc.). The reaction can be represented in the following general form:

$$(RO)_2P(O)-CH_2-COOR + R'R''C=O \rightarrow R'R''C=CH-COOR + (RO)_2P(O)OH.$$

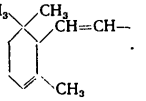
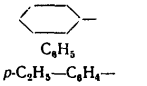
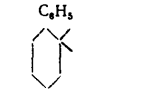
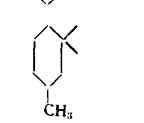
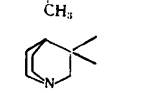
The Table gives the yields of the esters prepared in this way.

The P(O)-activated olefin synthesis with participation of phosphonoacetic ester and $\alpha\beta$-unsaturated ketones containing atoms or groups of atoms with pronounced electron-acceptor properties takes place particularly smoothly. Ketones of this kind have yielded a number of ethyl esters of γ-fluoro-substituted and other $\alpha\beta$-unsaturated acids [11]. For example:



Wadsworth and Emmons [96] proposed a simple method for the preparation of esters of α-substituted $\alpha\beta$-unsaturated acids in which a number of consecutive reactions are carried out in a single apparatus without isolating the intermediates. Phosphonoacetic ester in solution in 1,2-dimethoxyethylene

TABLE. Ethyl esters of $\alpha\beta$-unsaturated acids (R′R″C=CH–COOR) obtained from aldehydes and ketones by P(O)-activated olefin synthesis.

From aldehyde			From ketones			
R′ (R″=H)	yield, %	refs.	R′	R″	yield, %	refs.
CH_3	39	9	CH_3	CH_3	61	96,104
CCl_3	50	96	CH_3	CH_2Cl	58	105
			CH_3	CH_2Br	20	105
n-C_3H_7	67	104,106	CH_3	C_2H_5	58	9
$(CH_3)_2CH$	74	9,96	CH_3	$C(CH_3)_3$	15	9
$CH_2=CH$	14	9	CH_3	n-C_7H_{15}	43	9
			CH_3	n-C_9H_{21}	64	107
$CH_3-CH=CH-$	56	9,104	CH_3	$(C_2H_5O)_2CH-CH-$	31	108
$CH_3-(CH=CH)_2-$	53	9	CH_3	$(CH_3)_2C=CH-CH_2-CH_2-$ $-CH=C(CH_3)-CH_2-$	54	9,108
$CH_3-(CH=CH)_3-$	75	9	CH_3		44	9
$(CH_3O)_2CH-$	63	9	CH_3		35	109
C_6H_5	84	96,104,106	CH_3	C_6H_5	32	96,106
p-$O_2NC_6H_4-$	62	106	CH_3	*p*-$C_2H_5-C_6H_4-$	51	106
p-$(CH_3)_2C_6H_4$	81	106	C_2H_5	C_2H_5	64	96,107
$C_6H_5COO-CH=CH-$	72	9	C_6H_5	C_6H_5	87	104,107
$C_6H_5COO-(CH=CH)_2-$	51	9			70	16,107
$C_6H_5COO-(CH=CH)_3-$	60	9			70	107
	71	106			100	110

is successively metallated with sodium hydride, the resulting alkyl derivative is metallated again and finally condensed with the carbonyl compound. The preparation of the ester of α-n-butylacrylic acid (yield 60%), for example, can be described thus:

$$(RO)_2P(O)-CH_2-COOR + NaH \xrightarrow{-H_2} (RO)_2P(O)-CH(Na)-COOR \rightarrow$$

$$\xrightarrow[-NaBr]{+R'-Br} (RO)_2P(O)-CHR'-COOR \xrightarrow[-H_2]{+NaH} (RO)_2P(O)-CR'(Na)-COOR \longrightarrow$$

$$\xrightarrow{+CH_2=O} (RO)_2P(O)ONa + CH_2=C(R')-COOR \quad (R' = n\text{-}C_4H_9).$$

If after the first metallation stage bromine is introduced into the reaction mixture instead of an alkyl halide, the final reaction product is the ester of an α-bromo-αβ-unsaturated acid. For example, α-bromo-β-isopropylacrylic acid is obtained in this way (yield 65%):

$$(RO)_2P(O)-CH(Na)-COOR + Br_2 \rightarrow NaBr + (RO)_2P(O)-CH(Br)-COOR \longrightarrow$$

$$\xrightarrow{+NaH,\ (CH_3)_2CH-CHO} (CH_3)_2C=C(Br)-COOR + (RO)_2P(O)ONa.$$

If instead of bromine, iodine is used and the resulting iodophosphonate is further metallated and then condensed with a carbonyl compound, acetylene derivatives are obtained. For example, ethyl phenylpropiolate can be synthesised in this way (yield about 60%):

$$(RO_2)P(O)CHI-COOR + 2NaH + C_6H_5-CHO \rightarrow$$

$$\rightarrow C_6H_5-C\equiv C-COOR + H_2 + NaI + (RO)_2P(O)ONa.$$

The carbonyl groups of ketens can take part in P(O)-activated olefin synthesis as well as those of aldehydes and ketones. Under the conditions described above, (diethyl phosphono)acetic ester reacts with ethyl(phenyl)keten to give 1-ethoxycarbonyl-3-ethyl-3-phenylallene[96]:

$$(RO)_2P(O)-CH_2-COOR + NaH + C_6H_5(C_2H_5)C=C=O \rightarrow$$

$$\rightarrow H_2 + (RO)_2PO_2Na + C_6H_5(C_2H_5)C=C=CH-COOR.$$

Under these conditions ethyl levulinate reacts via its ketone group with (diethyl phosphono)acetic ester, forming 1,2-diethoxycarbonyl-2-methylbut-1-ene in good yield:

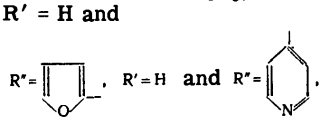
$$(RO)_2P(O)-CH_2-COOR + CH_3-CO-CH_2-CH_2-COOR + NaH \rightarrow$$

$$\rightarrow H_2 + CH_3-CH=C(COOR)-CH_2-CH_2-COOR + (RO)_2P(O)ONa.$$

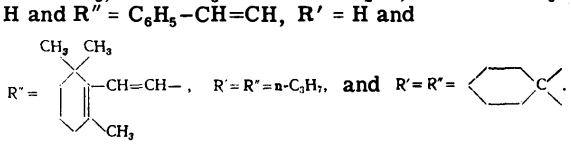
P(O)-Activated olefin synthesis has also proved valuable for the preparation of αβ-unsaturated acid nitriles which have recently become important in organic synthesis as intermediates in the synthesis of dyes, pharmaceutical preparations, and others. The nitriles are synthesised by condensing carbonyl compounds with the readily available diethyl ester of cyanomethylphosphonic acid. The following nitriles of αβ-unsaturated acids have been obtained in this way[96,103-105]:

$$(RO)_2P(O)-CH_2-CN + R'R''C=O \rightarrow R'R''C=CH-CN + (RO)_2P(O)OH,$$

where R' = R'' = H, R' = H and R'' = CH_3, R' = H and R'' = $CH_2=C(CH_3)$, R' = H and R'' = C_6H_5, R' = H and R'' = 2,6-$Cl_2C_6H_3$, R' = H and



R' = R'' = CH_3, R' = CH_3 and R'' = CH_2Cl, R' = R'' = C_6H_5, R' = H and R'' = C_6H_5–CH=CH, R' = H and



It has been found that the yields of the nitriles are quite satisfactory (60–80%) and the reaction takes place under mild conditions (at 20–50°) in various solvents (alcohols, toluene, xylene, dioxan, dimethylformamide) in the presence of different condensing agents (alkali metal hydroxides and alkoxides, the amides of alkali and alkaline-earth metals, and organic bases).

4. Isoprenoids and Compounds Related to Natural Substances

P(O)-Activated olefin synthesis can be used to prepare αβ-unsaturated carbonyl compounds. Thus the condensation of the ethyl acetal of (diethyl phosphono)acetaldehyde with benzaldehyde gives the diacetal of cinnamaldehyde which is smoothly hydrolysed to cinnamaldehyde itself[104]:

$$(RO)_2P(O)-CH_2-CH(OC_2H_5)_2 + C_6H_5-CHO + NaH \rightarrow$$

$$\rightarrow H_2 + (RO)_2P(O)ONa + C_6H_5-CH=CH-CH(OC_2H_5)_2 \xrightarrow[H^+]{H_2O} C_6H_5-CH=CH-CHO + 2C_2H_5OH.$$

The acetal $(RO)_2CH-CH_2-C(CH_3)=CH-COOR$ was obtained similarly[108] from phosphonoacetic ester and the diethyl acetal of acetoacetaldehyde.

Pommer[112] showed that P(O)-activated olefin synthesis gives better results in the preparation of carotenoids and related compounds than the Wittig olefin synthesis. Thus the synthesis of the dimethyl ester of crocetin (VI) takes place via a series of consecutive reactions, two of which are P(O)-activated condensations involving olefin synthesis. For this purpose, the tetraethyl ester of but-2-ene-1,4-diphosphonic acid (I) (yield 90%) is first prepared from 1,4-dichlorobut-2-ene and triethyl phosphite by the Arbuzov reaction and then condensed with two moles of methylglyoxal acetal (II). The resulting bisacetal of the C_{10} aldehyde (III) is hydrolysed to the C_{10} aldehyde (IV) itself. The latter is then condensed with the diethyl ester of 3-methoxycarbonylbut-2-enylphosphonic acid (V)† [the ester (V) is obtained by the Arbuzov reaction from the methyl ester of γ-bromotiglic acid and triethyl phosphite] to give the ester of crocetin (VI); the general mechanism of the synthesis can be represented by the following reactions:

$$(RO)_2P(O)-CH_2-CH=CH-CH_2P(O)(OR)_2 + 2(RO)_2CH-C(=O)-CH_3 \rightarrow$$

(I) (II)

$$\xrightarrow{2CH_3ONa} 2(RO)_2P(O)ONa + (RO)_2CH-C(CH_3)=CH-CH=CH-CH=C(CH_3)-CH(OR)_2 \longrightarrow$$

(III)

$$\xrightarrow[HCl]{H_2O} 4C_2H_5OH + O=CH-C(CH_3)=CH-CH=CH-CH=C(CH_3)-CH=O \quad (IV).$$

$$(IV) + 2H_3COOC-C(CH_3)=CH-CH_2-P(O)(OR)_2 \xrightarrow{+2CH_3ONa}$$

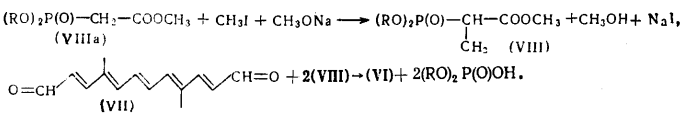
(V)

$$\longrightarrow 2(RO)_2P(O)ONa + H_3COOC\text{–}(CH=CH)_5\text{–}COOCH_3 \quad (VI).$$

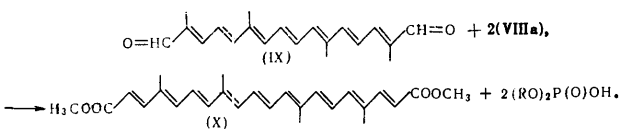
The same derivative of crocetin (VI) is obtained on condensing the C_{14} dialdehyde (VII) with the diethyl ester of α-methoxycarbonylethylphosphonic acid (VIII) which in turn is obtained by methylating the ester (VIIIa). Thus this method of the

† The C_{10} diol $CH_2OH-C(CH_3)=CH-CH=CH-CH=C(CH_3)-CH_2OH$ was obtained similarly from compound (I) and hydroxyacetone[112].

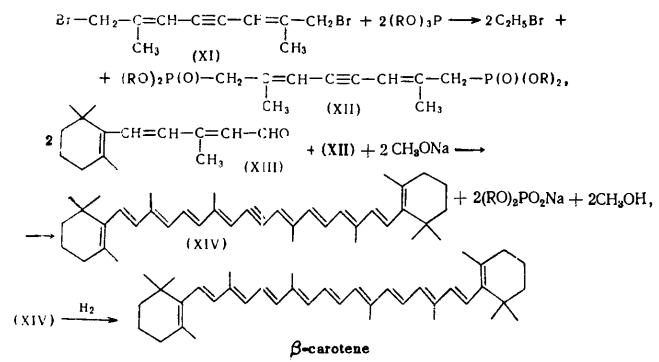
preparation of the diester (VI) can be described as follows:



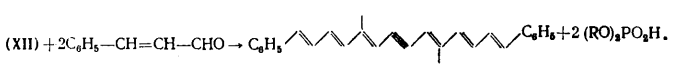
Similarly the condensation of the C_{20} dialdehyde (IX) with the ester (VIIIa) gave methylbixin (X):



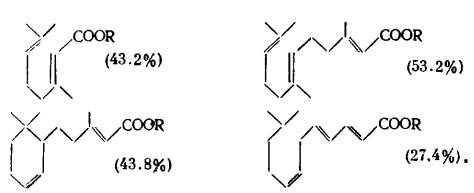
β-Carotene, the most important and most widely distributed plant pigment, was also prepared by P(O)-activated olefin synthesis. Pommer showed [112] that this method of synthesising β-carotene is superior, as regards the small number of stages and the availability of the starting materials, to all earlier procedures, including that involving the Wittig reaction [3]. The diethyl ester of 2,7-dimethylocta-2,6--dien-4-yne-1,8-diphosphonic acid (XII), prepared by the Arbuzov reaction from 1,8-dibromo-2,7-dimethylocta-2,6--dien-4-yne (XI) and triethyl phosphite, is condensed with two moles of β-ionylideneacetaldehyde (XIII) in the presence of sodium methoxide. The resulting 15,15'-dehydro--β-carotene (XIV) is smoothly converted into β-carotene after partial hydrogenation:



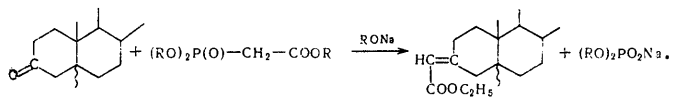
The ester (XII) reacts with cinnamaldehyde [113] by the usual mechanism of P(O)-activated olefin synthesis to yield the isoprenoid olefin 5,10-dimethyl-1,14-diphenyltetradeca-1,3,5,9,11,13-hexaen-7-yne:



By condensing phosphonoacetic ester with methylheptenone, geranylacetone, α-ionone, and α-dihydroionone in dimethylformamide in the presence of sodium methoxide, Kovalev et al. [108] obtained a number of esters of isoprenoid acids (yields are given in brackets):



The use of P(O)-activated olefin synthesis in the steroid series appears to be promising. The work of Bose and coworkers shows that 3-oxosteroids react via the carbonyl group with phosphonoacetic ester to form ethoxycarbonylmethylene derivatives [114]:



The data compiled in the present review on the methods of preparation, properties, and applications of P(O)-activated reagents for olefin synthesis show that this new method permits relatively simple preparation of unsaturated compounds with a specified structure; the compounds may belong to different classes and may be of various complexity. It is noteworthy that the possibilities of P(O)-activated olefin synthesis have been by no means exhausted as regards application to syntheses involving many organic compounds with carbonyl groups. There is no doubt that further studies in this field will yield new results of value for organic synthesis.

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SYNTHETIC OPTICALLY ACTIVE POLYMERS

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I. INTRODUCTION

Recently a new field of study has arisen in the chemistry of monomers, associated with the synthesis of optically active polymeric substances. Their synthesis and the study of their properties are of great theoretical and practical interest. From the theoretical standpoint, asymmetric synthesis of polymers constitutes a higher type of control of stereoregularity, compared with the synthesis of the usual regular crystalline polymers. It represents a further advance in the control of the synthesis of macromolecular materials. The synthesis of optically active polymers has introduced into polymer chemistry a new parameter — the specific rotation of polymers which is due to the presence of uncompensated asymmetry and constitutes the overall stereochemical result of the reaction. The studies of the changes in the optical rotation of the polymer as a function of polymerisation conditions makes it possible to establish the relation between the specific rotation, structural regularity, and the molecular weight of the polymer. Investigation of the optical activity of the degradation products of optically active polymers can reveal the steric relations which obtain between the monomer, the catalytic system, and the polymer.

On the other hand, successful synthesis of optically active polymers in the presence of small amounts of an asymmetric cocatalyst constitutes a first approximation to the modelling of processes in nature, where protein molecules are formed in the presence of small amounts of highly specific enzymes as a result of a series of complex consecutive reactions.

Since optically active polymers and oligomers have highly specific structures, they may prove important as components of very selective catalysts in polymerisation and polycondensation processes and they may also be used in the asymmetric synthesis of small molecules, as model systems in the study of biocatalysis, and as adsorbents for the separation of racemic mixtures.

Optically active polymers prepared from optically active monomers exhibit improved mechanical properties and thermal stability compared with polymers synthesised from the analogous racemic monomers, which is of undoubted practical interest. In recent years optically active polymers have been increasingly attracting the attention of investigators. This interest was stimulated, on the one hand, by the study of the structural features of proteins and nucleic acids in solutions and, on the other hand, by the advances in stereospecific polymerisation. Up to 1956 there were only seven papers on optically active polymers, while in 1961 alone about thirty publications appeared, including a number of reviews [1-4].

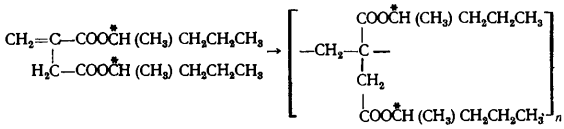
There exist three fundamental approaches to the study of optically active polymers. One of them is associated with the determination of the laws governing the asymmetric synthesis of macromolecular substances, the second deals with the study of the properties of optically active polymers, and finally, the third is concerned with the application of optically active labels in experiments designed to solve a wide range of problems in polymerisation chemistry: elucidation of the nature of active centres in catalytic systems, the conformation of macromolecules in solution, the microtactic properties of chains, the polymerisation kinetics, etc.

The author has attempted to elucidate mainly the first and the last of these problems. She wished to demonstrate the wide variety of possible uses of the optically active label; by virtue of its simplicity and availability, the procedure based on such labelling will undoubtedly form part of the arsenal of the methods available in polymer chemistry.

II. SYNTHESIS OF OPTICALLY ACTIVE POLYMERS FROM OPTICALLY ACTIVE MONOMERS AND THEIR PROPERTIES

There is nothing new in the polymerisation of optically active polymers compared with the usual stereospecific polymerisation apart from the use of the optically active monomers themselves. The resulting polymer is optically active only if the reaction does not involve the asymmetric centres of the molecule and hence racemisation does not take place.

In 1896 Walden[5] achieved the polymerisation of the optically active ester of itaconic acid, in which the asymmetric carbon atoms are located in the ester groups:



The optical rotation of the polymer is of the same order of magnitude as that of the monomer.

1. Optical Activity of High-Molecular Compounds

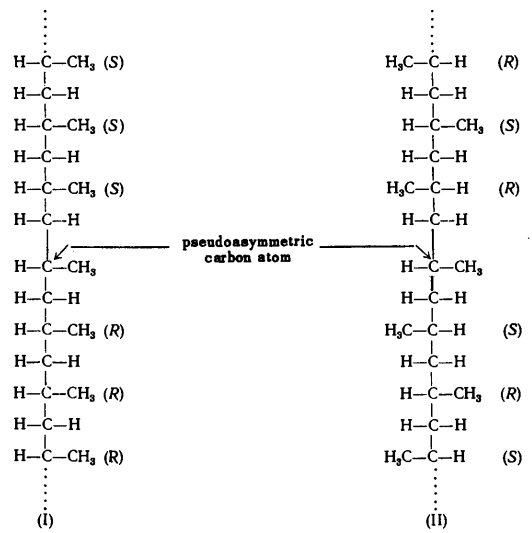
The optical activity of polymers is usually expressed in terms of the specific rotation $[\alpha]$ and the molar rotation $[M]$ which are defined by the following formulae:

$$[\alpha] = \frac{\alpha \cdot 100}{l \cdot c}; \quad [M] = [\alpha] \cdot \frac{M}{100},$$

where α is the measured angle of optical rotation (in degrees), l the thickness of the layer of substance (in decimeters), c the concentration of the solute (in grammes per 100 ml of solution), and M the molecular weight of the polymer unit.

It should be borne in mind that the observed optical activity is a fairly complex sum of contributions due to different factors. The principal factors are as follows: optically active side groups, the primary structure determined by the covalent bonds in the chain or the configuration of the macromolecule, and the secondary structure (or chain conformation) determined by steric, non-valence interaction of the side-group.

Consideration of the chain of stereoregular polymers of the vinyl type $(-CH_2-CHR-)_n$ readily shows that, owing to the stereochemical characteristics of the asymmetric carbon atom in the main chain, the primary structures in both iso- and syndio-tactic polymers are symmetrical and cannot contribute to the optical rotation of the polymer. Indeed the chain of the syndiotactic polymer (II) formed by a regularly alternating sequence of (*R*)- and (*S*)-configurations of the asymmetric atoms† is internally compensated. In the case of the isotactic sequence of chain units (I) the asymmetry of the carbon atoms in -CHR- groups is due to the differences in the lengths of the segments of the polymeric chain joined to them. Since the immediate environment of the asymmetric atoms in each -CHR- group (apart from those nearest to the ends of the chain) is almost symmetrical, such polymers have numerous symmetry planes and are therefore optically inactive.

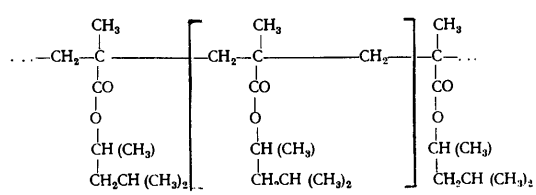


An atactic polymer formed by randomly alternating (*R*)- and (*S*)-asymmetric centres constitutes a random "meso-form" which cannot possess optical activity.

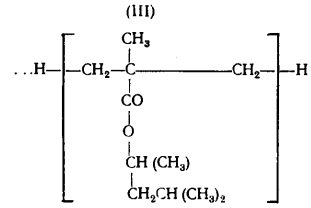
Thus comparison of the optical activities of polymer solutions with the rotation of the monomers or model compounds makes it possible, in principle, to determine the conformational contribution to the rotation and to assess on this basis the nature of the secondary structure of the macromolecule in the solution.

2. The Use of Optically Active Monomers in the Determination of the Conformation of Macromolecules in Solution

The first attempt to analyse the rotatory power of polymers was made by Arcus and West[6], who compared the optical activity of the polymers of 1,3-dimethylbutyl (+)-methacrylate (III) with the activity of the model compound 1,3-dimethylbutyl pivalate (IV). The algebraic difference between the molar rotations of the polymer and the model compound proved to be negative and equal to one third of the rotation of the model compound. The authors suggested that the observed change in rotation is associated with the presence of helical sections in the macromolecules in solution:



(III)



(IV)

† For the nomenclature, see E. L. Eliel, "Stereochemistry of Carbon Compounds" (Translated into Russian), Izd. Mir, Moscow, 1965 [McGraw-Hill, 1962].

Natta and coworkers[7] showed that in the crystalline regions all isotactic polyolefins exist in the form of rigid right- and left-hand helices. In the polymerisation of olefins without optically active side-groups, the amount of different enantiomorphic forms of the helices is the same and therefore the polymer as a whole is optically inactive. On the other hand, if the polymer is crystallised under conditions which favour the preferential formation of a particular type of helix, such structures acquire optical activity[8]. Dissolution of a crystalline polymer results in the breakdown of long, well formed helices. It has been demonstrated experimentally[9] and theoretically[10] that small sections with helical conformations persist also in solution, i.e. the one-dimensional short-range order in the macromolecules in solution is in most cases similar to the one-dimensional long-range order in the crystalline state. The maintenance of one-dimensional long-range order in a free macromolecule requires the presence of intramolecular forces capable of resisting the disorienting effect of thermal motion. In polypeptides such forces are the hydrogen bonds between the repeating CO and NH groups which ensure a rigid helical structure of the macromolecules in solution[11]. The forces of steric repulsion between groups cannot by themselves fix rigidly the position of the units of the main chain and prevent the macromolecule from rolling up into a randomly twisted spherical structure.

In their study of poly-α-olefins with optically active side-groups, Pino[12-15], Bailey[16], and Nozakura[17] found that the polymers had a considerably higher optical activity than the monomers (Table 1). The absolute magnitude of the molar optical activity of the isotactic fractions of the polymers is more than ten times greater than the molecular rotation of the analogous low-molecular compounds. The sign of the optical activity of the poly-α-olefins investigated is determined by the absolute configuration of the asymmetric carbon atom of the monomer: all the polymers of (*S*)-α-olefins exhibit positive rotation while the polymers of (*R*)-α-olefins exhibit negative rotation. Goodman and Abe[18-20] observed a similar increase, compared with the monomers, in the optical activity of polymers based on aldehydes and containing the same optically active substituents as the poly-α-olefins discussed above. Very interesting results were also obtained by Ciardelli at al.[21], who reduced the optically active poly-4-methylhex-1-yne with $[\alpha]_D = +2.0°$ to poly-4-methylhexene with $[\alpha]_D = +178°$.

TABLE 1. Comparison of the optical activities of model saturated hydrocarbons with the optical activities of atactic and isotactic fractions of certain poly-α-olefins.*

Low-molecular saturated hydrocarbons	$[M]_D^{25}$	Polymer	$[M]_D^{25}$ amorphous or very weakly crystalline fraction	$[M]_D^{25}$ highly crystalline fraction
(*S*)-2,3-dimethylpentane	−11.4	poly-(*S*)-3-methylpent-1-ene	+29.4	+161
(*S*)-2,4-dimethylhexane	+21.3	poly-(*S*)-4-methylhex-1-ene	+116	+288
(*S*)-2,5-dimethylheptane	+11.7	poly-(*S*)-5-methylhept-1-ene	+13.1	+68*
(*S*)-3-methyloctane	+13.3	poly-(*S*)-6-methyloct-1-ene	+12.8	+20*
(*S*)-2,6-dimethyloctane	+14.4	poly-(*R*)-3,7-dimethyloct-1-ene	−20.6	−154

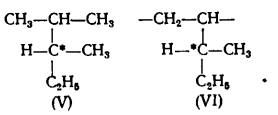
* These data refer to the most isotactic of the soluble fractions.

Pino and coworkers explain the very high optical activities of the poly-α-olefins on the basis of the above hypothesis that there is a helical short-range order in the macromolecules of isotactic polymers. When isotactic poly-α-olefins are formed, left- and right-hand helices are not energetically equivalent, since different sets of conformations of the side-group and different energies of these conformations correspond to a particular configuration of the asymmetric carbon atom in the substituent in the right-hand and left-hand helices and therefore one of the helical forms predominates in the polymers. Calculation of the molar rotation of polymers carried out in one of Pino's studies[14] by Brewster's semiempirical method[22] showed that the sign of the observed optical activity is consistent with the sign of the optical activity calculated for the helical conformation which is associated with the greatest number of rotational isomers in the side-group, i.e. has the smallest free energy.

In view of the approximate nature of the calculations by Brewster's method, the authors were unable to decide finally whether the agreement between the calculated and observed values of $[M]$ is fortuitous or real.

Birnshtein and Luizi[23] made a theoretical study of the conformational structure of the optically active poly-α--hydrocarbons which had been investigated by Pino. They showed that in macromolecules where short-range order extends over several monomer units even a small difference in the free energies of the right- and left-hand helices is sufficient to ensure that the helical conformation of lower energy predominates in the statistically twisted chains.

To elucidate the reasons for the higher optical rotation of polymers, we shall consider, from the standpoint of the conformations, the conversion of a model low-molecular optically active hydrocarbon (V) into a polymeric chain (VI):



(V) (VI)

In low-molecular hydrocarbons the number of possible conformations is fairly large and the magnitude of optical rotation is determined by the algebraic sum of positive and negative conformational rotational contributions which are of a similar value[22]. On conversion to the high-molecular compound at least one of the monomer conformations is "frozen". As a result, the equilibrium constants governing the relative amounts of dextro- and laevo-rotatory conformations in isotactic polymers and low-molecular saturated hydrocarbons differ significantly. The chromophore system of the polymer is the same as that of the monomer. The only chromophore group in these compounds is the C–H bond at the asymmetric carbon atom in the side-group. The maximum number of units in frozen conformations occurs in a helical structure, since the latter corresponds to minimum free energy.

Thus the high values of the optical rotation of poly-α--olefins are associated with the formation of preferred conformations (rigorous steric requirements) at the asymmetric atoms of the side-groups which leads to the formation of left- or right-hand helices. Pino's hypothesis does not contradict the explanation of the high values of the rotation of polymers, compared with the low-molecular

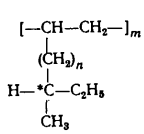
compounds, put forward by Goodman and Abe[20], who believe that the conformational rigidity of polymeric chains is due to the excess of one type of *gauche*-conformation over the others for a given isotactic sequence.

It is interesting to compare the characteristic features of the optical rotation of poly-α-olefins with the rotation of synthetic polypeptides. By virtue of the asymmetry of the helical structure itself, polypeptides, which are present in solution in a spiral conformation, behave optically as a single absorbing system and make a special "helical" contribution to the overall rotation. The optical rotary dispersion of polypeptides in solvents which do not cause appreciable breakdown of hydrogen bonds does not obey Drude's single-term equation[24] but is described by more complex expressions. The factors which influence the conformation of polypeptides (solvent, temperature, concentration of polymer, etc.) also cause a change in the optical rotation of their solutions.

In contrast to polypeptides, the optical rotatory dispersion of polyhydrocarbons in the wavelength range accessible to measurement does obey Drude's simple equation. The concentration[15] of the polymer and the solvent have little effect on the optical rotation. It is noteworthy that the temperature coefficients $\Delta[M]/\Delta T$ for polyhydrocarbons are fairly large (between -0.2 and -0.65) and depend on the stereoregularity of the fractions: they are larger for crystalline structures than for the less regular fractions.

This difference in the behaviour of the optical rotation of these two classes of "helical" polymers can be explained by the fact that the only chromophore group in polyhydrocarbons is the C–H bond at the asymmetric carbon atom in the side-group, whereas in polypeptides the chromophore system of the CO–NH unit linked by hydrogen bonds is located in the main chain. Naturally the factors which influence the stability of the hydrogen bonds in polypeptides cannot affect the conformational composition of optically active poly-α-olefins.

The optical activity of poly-α-olefins depends significantly on their stereoregularity, which is also consistent with the hypothesis of the helical structure of the polymers in solution. Comparison of the optical rotation of the most stereoregular fractions of polymers with the general formula (VII),



(VII),

where n = 0, 1, 2, and 3 shows that the molar rotation is very high for poly-(*S*)-3-methylpent-1-ene (n = 0), reaches a maximum for poly-(*S*)-4-methylhex-1-ene (n = 1), but falls appreciably in the case of higher homologues (Table 1).

Thus the study of the optical activity of polymers in solution is a very sensitive qualitative method, whereby it is possible to demonstrate whether or not sections of the helical structure of isotactic macromolecules persist in solution. Probably the secondary structure of the polymer itself influences the stereoregularity in the course of further polymerisation. Thus in the polymerisation of α-amino-acids such "stereoregulating" influence may arise on formation of an α-helix in which the isotactic distribution is preferred to the atactic distribution as a result of the better steric accommodation of the R-groups in the repeating structural unit *CHR–CONH.

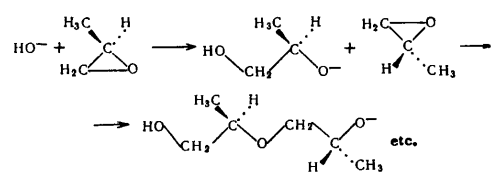
It has been shown experimentally that addition of the D-isomer in the polymerisation of the anhydride of γ-benzyl-*N*-carboxy-L-glutamic acid[11], catalysed by sodium hydroxide, decreases sharply both the rate and degree of polymerisation. This can be explained by the difficulty of incorporation of the D-isomer of the amino-acid as a unit in the growing α-helix formed from the L-amino-acid. In fact the decrease in rate is so considerable that it suggests not only that the unnatural amino-acid fails to be incorporated in the polymer chain but also that the growing chain is partially blocked on encountering the "foreign" monomer. Minoru[25] synthesised polymers by esterifying poly(vinyl alcohol) with an optically active acylamino-acid and determined the dependence of the optical activity on the degree of polymerisation and esterification. He found that the optical activity attained on introduction of a single optically active residue into the side-chain of the polymer is almost constant and independent of the degree of polymerisation and esterification of poly(vinyl alcohol).

In his study of the copolymers of styrene and (-)-menthyl acrylate, Schulz[4] found a rigorous proportionality between the optical activity and the content of the optically active component. This led him to the conclusion that there is no mutual influence of the asymmetric units in the chain. Thus the rotation of polymers and copolymers present as randomly twisted structures in solution may be used to determine their analytical composition.

The synthesis of optically active polymers containing asymmetric non-carbon atoms is of considerable interest. The only study in this field is the synthesis of the optically active poly-(+)-vinylphenyl-α-naphthylsilane achieved by Davydova et al.[26]; unfortunately the properties of the polymer are not described.

3. Polymerisation of Optically Active Propylene Oxide

One of the most thoroughly investigated optically active polymers is poly(propylene oxide) which was synthesised by Price et al. in 1956.[27] They showed that the polymerisation of the L-enantiomorph of propylene oxide takes place by an S_N2 mechanism in the presence of potassium hydroxide, first hydroxide and then alkoxide ions behaving as nucleophilic agents:



The reaction results in the formation of a fully crystalline isotactic polymer. In the presence of ferric chloride, however, a mixture of optically active crystalline and inactive amorphous polymers is obtained. Thus in the polymerisation in the presence of potassium hydroxide asymmetry is preserved to a high degree, while ferric chloride causes partial racemisation which is due to the rupture of the bond between the asymmetric carbon atom and oxygen.

Studies on the stereospecific polymerisation of propylene oxide and the relations between the type and structure of heterogeneous catalysts and the properties of the resulting polymers are of considerable interest. In this case an optically active label can also prove useful. The preservation or loss of optical activity on polymerisation of different enantiomorphs, the variation of the stereoregularity of the resulting polymers with the optical "purity" of the monomer, and also the relative rates of polymerisation of racemic and optically active propylene oxide permit the solution of a number of problems associated with the mechanism of stereoregulation (including the site where the epoxide ring is ruptured), with the chemical and stereochemical homogeneity of the active centres of the catalyst, etc.

The possible difference in the rates of polymerisation of racemic and optically active monomers was first pointed out by Kulkarni and Morawetz[28] in the polymerisation of methacryloyl and acryloyl derivatives of certain amino-acids (alanine and glutamic acid). However, a difference in the rates of polymerisation was actually observed in only one case: methacryloyl-DL-glutamic acid polymerised in the presence of benzoyl peroxide at a rate which was smaller by 5.6% than that of the polymerisation of the optically active compound.

Krylov and Livshits[29] made a theoretical analysis of the relative rates of polymerisation of the racemic monomers and the corresponding optically active compounds assuming different orders of the reaction with respect to the monomer. They demonstrated convincingly that in the stereospecific polymerisation of propylene oxide in the presence of magnesium oxide or oxalate as catalysts both enantiomorphs polymerise at the same rate which, for a first-order reaction, is twice as high as in the polymerisation of the racemate. This shows that, as was to be expected, the catalyst contains stereochemically indistinguishable centres.

To elucidate the mechanism of the asymmetrically induced polymerisation of propylene oxide on dialkylzinc–alcohol catalysts, Tsuruta et al.[30] studied the polymerisation of the monomer with different proportions of the D- and L-enantiomorphs. For comparison, the D- and L-enantiomorphs of propylene oxide were copolymerised in the presence of potassium hydroxide which is known to be a non-stereospecific catalyst. It was found that the plot of $[\alpha]_D$ for the polymer against $[\alpha]_D$ for the initial monomer is linear, both for the diethylzinc–methanol system and for potassium hydroxide. In both cases the rotation of the unreacted monomer was equal to that of the initial monomer regardless of the degree of polymerisation. To account for these results, the authors suggested that the catalytic system diethylzinc–alcohol contains two types of catalytic centre (D and L), but this cannot be regarded as evident even under the condition that "the racemisation which may occur when the monomer is incorporated in the polymer chain in the presence of the organozinc catalyst is of the same extent as in the presence of potassium hydroxide". It is interesting that the acetone-insoluble crystalline fraction of the polymer obtained on the organozinc catalyst has a higher value of $[\alpha]_D$ than the unfractionated polymer, while the soluble fraction has a lower value. The authors attribute this phenomenon to the preferential incorporation of the D-enantiomorph of propylene oxide in the crystalline polymer, so that its proportion is higher than in the initial monomer, but this is inconsistent with the hypothesis of the symmetrical distribution of the catalytic D- and L-centres.

Optically active polymers have also been obtained from propylene lactide[31], propyleneimine[32], conidine[33], and substituted caprolactams[34,35].

4. Effect of the Microtactic Structure of Macromolecules on the Optical Rotation of the Polymers

The use of optically active monomers gives rise to the possibility of a new approach to the study of the microstructure of the resulting polymers. Studies in this field have been begun recently by Schulz and Hilpert[36] who obtained a number of (-)-poly(bornyl acrylates) under conditions of radical and ionic polymerisation and investigated the curves representing the variation of the optical rotatory dispersion (ORD curves) of the polymers. Previously ORD curves were used mainly to observe the increase in the optical rotation of the polymers in the short-wavelength part of the spectrum, this serving as an indication of asymmetric synthesis of the macromolecules[37,38]. However, these curves can also provide useful information about the microstructure of the optically active polymers.

Klabunovskii et al.[39] used the data of Arcus and West[6] to find the constants A and λ_0 in the Drude equation. We may recall that the Drude equation is

$$[\alpha]_\lambda = \frac{A}{\lambda^2 - \lambda_0^2},$$

where λ_0 is the wavelength corresponding to the optically active electronic transition, λ the actual wavelength used, A the rotational constant proportional to the rotatory power associated with the transition, and to $(n^2 + 2)/3$, where n is the refractive index of the solvent.

It was shown that variation of the duration of the reaction, polymerisation temperature, and the molecular weight of (+)- and (-)-poly(1,3-dimethylbutyl methacrylates) changes slightly the rotational constant A but has no effect on λ_0. The radical initiator used has almost no influence on A and λ_0.

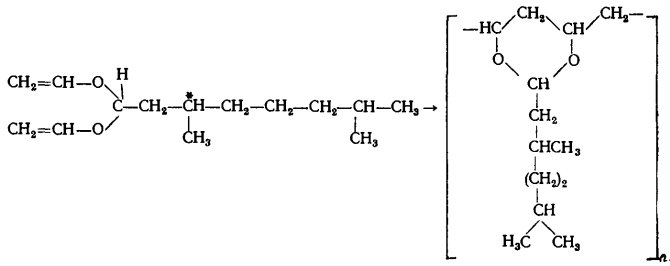
The spectropolarimetric method has been used to study the structure of polymers obtained by radical and anionic polymerisation of (+)-2-methylbutyl methacrylate[39]. It was found that λ_0 for polymers is close to the value for the monomer (about 190 nm). The values of A for the polymers obtained by radical and anionic mechanisms are significantly different and consistent with the data of Arcus and West[6].

However, Klabunovskii et al.[39] arrived at the incorrect conclusion that the stereoregularity of the polymer obtained by the radical mechanism is higher than that of the polymer obtained in the presence of a Grignard reagent. This was shown by Japanese investigators[40] in infrared and NMR spectroscopic studies of poly(methacrylic acid) obtained by the hydrolysis of the corresponding esters. By a similar treatment of ORD curves for propylene oxide polymers synthesised from L- and D-enantiomorphs in chloroform and methanol, Livshits[41] showed that the experimental curves are described by the Drude single-term equation. Polymers with greater stereoregularity give rise to higher values of A, determined by the optical activity at the sodium D-line.

The experimental data available at the present time are inadequate for the determination of the variation of the parameters defining the ORD curves as a function of the

stereoregularity of the polymers. To obtain more accurate values of the optical rotation, a correction for the dispersion of the refractive index of the medium must be applied to the observed specific rotation $[\alpha]$. Then the differences in the value of A should be consistent with the differences in the overall rotatory power associated with the optically active electronic transitions in polymers of various stereoregularities.

Abe and Goodman[42] showed that, depending on the method of polymerisation of the divinyl acetal of (+)-3,7-dimethyloctanal, the sign of the optical rotation of the resulting polymers can change:



A low-molecular polymer with optical activity close to that of the monomer and the model compound diethyl acetal of (*R*)(+)-citronellal was obtained by radical polymerisation. Cationic polymerisation in the presence of boron trifluoride–ether or aluminium chloride–ether gives solid high-molecular products with rotation of the opposite sign in the same solvent. It is interesting that the optical rotation of these polymers, like that of the (-)-poly(propylene oxide), decreases on going from benzene to chloroform solutions.

The authors attribute the difference in the rotation of substituted polydioxans to the different stereoregularity of the polymers. In this case it is reasonable to expect that the polymer obtained by the cationic mechanism has the greater stereoregularity.

The converse is also true, namely that polymers with the same chain microstructure should have the same optical rotation. Schulz[4] found that the optical activity of polyacrylates obtained by the radical mechanism and under the action of γ-radiation at -8° is the same. On this basis, he arrived at the incorrect conclusion that the polymerisation of acrylic acid esters in the amorphous, vitreous state under the action of γ-radiation involves a radical mechanism. Here the equality of the optical rotations of the polymers implies only that the microtactic structure of the chains is the same and that in both cases the polarisation is probably equally non-specific.

5. The Use of the Optically Active Label in the Study of Polymerisation Kinetics

In their study of the radical polymerisation of optically active (+)-s-butyl β-chloro(β-bromo)acrylates and vinyl (-)-β-phenylbutyrate in 1940, Marvel et al.[43] observed that the polymers have rotations which differ from those of the initial monomers by 9–12°. This difference was used to study the polymerisation kinetics.

Klabunovskii et al.[44] used a polarimetric method to study the kinetics of the radical polymerisation of the optically active esters of methacrylic and itaconic acids. The polarimetric study of polymerisation kinetics in homogeneous solutions may prove of value in certain cases, provided that the specific rotations of the monomer and the polymer differ appreciably.

III. SYNTHESIS OF OPTICALLY ACTIVE POLYMERS FROM OPTICALLY INACTIVE MONOMERS

1. The Concept of the Asymmetric Synthesis of Macromolecules

The asymmetric synthesis of macromolecules implies that in polymerisation induced by asymmetric agents there is either a selection of one enantiomorph from a monomer which consists of a racemic mixture and a fixation of these configurations in the polymer chain or formation of new asymmetric centres with a definite configuration on dissociation of a double bond or ring opening and their fixation in the macromolecular chain.

As in the case of low-molecular substances, asymmetric synthesis or asymmetric induction‡ of macromolecules can be divided into absolute and partial. By absolute asymmetric synthesis, the present author understands the synthesis of optically active substance in the absence of other optically active chemical agents (for example, under the action of circularly polarised light). Asymmetric syntheses involving the participation of auxiliary optically active substances are called partial asymmetric syntheses.

Together with partial asymmetric synthesis, in which new asymmetric centres are induced by asymmetric agents, it is also necessary to distinguish asymmetric kinetic separation. The latter term means preferential conversion or decomposition in a given reaction of one of the components of a racemic mixture because this component is formed or reacts more rapidly than the other. This follows from the fact that the two transition states are diastereoisomeric, their free energies of formation being different.

In connection with the polymerisation of racemic monomers, this means that, in the presence of optically active catalysts, preferential formation of one of the following two enantiomorphic chains is possible:

$$(R+S)\xrightarrow[\text{catalyst}]{\text{optically active}}\text{or}\ \begin{matrix}RRRR\ \ldots\\ SSSS\ \ldots\end{matrix}.$$

The unreacted monomer becomes enriched in the enantiomorph of the opposite sign to that incorporated in the chain. This type of polymerisation is called stereoelective[45].

When a racemic monomer is copolymerised with one of the enantiomorphs of another monomer, two chains can be formed, one of which contains only monomers in the (*R*)-configuration and the other only monomers in the (*S*)-configuration, i.e. a copolymer (*RRR*'...) and a homopolymer (*SSS*...) are formed:

$$(R+S)+R'\text{–}\begin{matrix}\nearrow RRR'R'R'RR\ \ldots\\ \searrow SSSSS\ \ldots\end{matrix}.$$

‡ There is no agreement in the literature concerning the use of these terms. In the present review they will be used to indicate the formation of both a new asymmetric atom and asymmetric molecular chains under conditions in which two stereoisomers are formed in unequal amounts.

This unusual type of copolymerisation is called stereoelective copolymerisation[45]. Stereoselective polymerisation must be distinguished from stereoelective polymerisation; the former consists in the polymerisation of racemic monomers in the presence of symmetrical catalysts with separation of the enantiomorphs during polymerisation and the formation of two enantiomorphic chains:

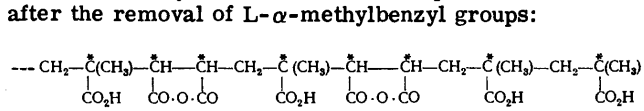
$$(R+S)\begin{cases}\nearrow RRRR\ldots\\ \searrow SSS\ldots\end{cases}$$

2. Asymmetric Synthesis of Macromolecules

Only one unsuccessful attempt to achieve absolute asymmetric synthesis, in the photo-polymerisation of styrene and copolymerisation of styrene with maleic anhydride under the action of polarised β-radiation[46], has been described. One of the possible ways of achieving partial asymmetric synthesis consists in the polymerisation of a monomer, which is optically active due to a substituent, with subsequent removal of the optically active side-groups from the final polymer. The question then arises how the optically active side-groups of the monomer influence the stereospecificity of the polymerisation. If the optically active monomer is the first unit of the growing chain, the next unit can add on either in the iso-position (DDD- or LLL-, where D and L represent the configurations of the asymmetric carbon atoms in the main chain) or in the syndio-position (DLD- or LDL-). The adducts of the monomer and the initiating radical or ion are no longer enantiomorphs but diastereoisomers, the rates of formation of which are always different. Thus the presence of optically active groups in the monomer gives rise to the potential possibility of the formation of a polymer with an optically active main chain. Whether or not the polymer or copolymer is optically active after the removal of the optically active side-groups depends on the symmetry or asymmetry of the chain formed. This problem was discussed in detail in section I, where it was shown that the primary structures of vinyl polymers are symmetrical. The secondary structure also becomes symmetrical after the removal of the optically active groups.

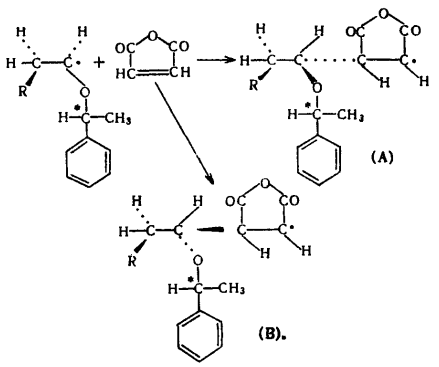
The numerous attempts to prepare optically active polymers in this way proved to be unsuccessful. Thus homopolymerisation of (+)-fluorobutyl *p*-vinylbenzoate[47], (+)-*o*-(s-butylthiomethyl)styrene[48], and (-)-1-phenylethyl methacrylate[49] and the copolymerisation of (+)-*o*-(s-butylthiomethyl)styrene with methyl methacrylate[48], followed by the removal of the optically active groups, yielded optically inactive products.

The simplest possibility of asymmetric induction is the copolymerisation of any optically active monomer with a second monomer, a disubstituted olefin, in which asymmetric carbon atoms can arise during the reaction. The copolymerisation of a usual vinyl monomer with a disubstituted olefin gives rise to three asymmetric atoms with four different substituents in its immediate vicinity. Using an optically active comonomer, it is possible to control the configuration of the induced asymmetric atoms. Thus using radical initiation, Beredjick and Schuerch[49] obtained a copolymer of L-α-methylbenzyl methacrylate and maleic anhydride which exhibited positive rotation after the removal of L-α-methylbenzyl groups:



Schmitt and Schuerch[50] obtained a laevorotatory copolymer (28.5°) by the free-radical copolymerisation of maleic anhydride with L-α-methylbenzyl vinyl ether.

The mechanism of asymmetric induction can be represented as follows:



Immediately after the first step involving the addition of two comonomers two diastereoisomeric radicals (A) and (B) are formed regardless of the configuration of the asymmetric carbon atom in the side-chain of the active component. For this reason, the rates of their formation (and further growth) must be different. During polymerisation one of the configurations of the induced asymmetric atoms is formed in excess and the corresponding copolymer exhibits optical activity even after the removal of the asymmetric side-groups. The attempt to achieve asymmetric synthesis with the aid of optically active acyl peroxides resulted in the formation of optically inactive polymers[51]. Frisch et al.[52] demonstrated theoretically that under the conditions chosen the effect of the asymmetric catalyst weakens after several chain-growth steps and therefore the specific rotation of the polymer decreases with increase in the degree of polymerisation. The situation is different in those cases where in each chain-growth step the asymmetric agent is near the growing end. This type of selection of the monomer with a specified configuration, as it approaches the growing end of the polymer chain, can be achieved by selective adsorption of the monomer on the surface or the formation of asymmetric complexes. Thus a surface or complexing agents are very important for asymmetric synthesis.

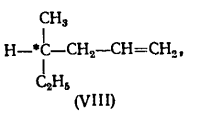
In their study of the theoretical aspects of asymmetric synthesis, Frisch et al.[52] analysed two different modes of asymmetric induction. In the first hypothesis (hypothesis of asymmetric initiation) it is assumed that the asymmetric agent influences only the first addition step and induces the formation of D-enantiomorphs with a probability different from that of the formation of the L-enantiomorphs. After the first addition step the probability of the persistance of the D- and L-configurations is the same, $k_{DD} = k_{LL}$ but $k_{DD} \neq k_{DL}$, where k_{DD}, k_{LL}, and k_{DL} are the rates of formation of the sequences DD, LL, and DL. In this case the optical activity of the polymer is inversely proportional to chain length and tends to zero for polymers with a high molecular weight.

The second hypothesis (hypothesis of asymmetric growth) postulates chain growth such that in each growth step the probability of addition in a given sequence is different from that in another sequence ($k_{DD} \neq k_{LL}$). The optical activity is independent of molecular weight and directly

proportional to the degree of asymmetric induction transmitted by the catalytic system. Qualitatively asymmetric induction should be most effective when the difference in the size of the substituents at the asymmetric centre of the molecule is large and the induced centre is as close as possible to the one already present.

3. Polymerisation of Racemic Monomers on Optically Active Catalysts

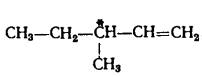
To assess the first hypothesis of asymmetric induction, Pino[53] studied the polymerisation of racemic 4-methylhex-1-ene (VIII),



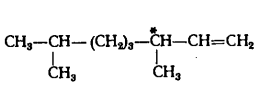
(VIII)

on a complex catalyst (based on titanium tri- and tetrachloride and optically active organometallic compounds) and compared the optical activities of the resulting polymers with the optical activity of certain polypropylene and polystyrene fractions prepared in the presence of the same catalysts. In the case of polypropylene and polystyrene only low-molecular fractions proved to be active, the optical activity decreasing rapidly with increasing molecular weight of the fraction. The optical activity of the low-molecular polymers of 4-methylhex-1-ene was much higher than that of the styrene and propylene polymers but smaller by a factor of 10–100 than the value for the optically active poly-(*S*)-4-methylhex-1-ene. The unreacted monomer proved to be inactive. The most likely explanation of the low activity of the polymers is that the optically active alkyl group of the catalyst or the first monomer unit do not determine the type of enantiomorph selected preferentially for the construction of the macromolecule, i.e. both monomer enantiomorphs are polymerised at almost the same rate. At the same time the optical activity of poly-4-methylhex-1-ene fractions obtained in the presence of catalysts based on the optically active zinc alkyl Zn(iso-C_5H_{11})$_2$ and titanium tetrachloride proved to be very high. Probably here the optical activity is not determined solely by that of the catalyst group but also by the asymmetric induction due to the first monomer unit.

The chemical structure of the monomer has a significant effect on the type of asymmetric induction. Thus in the polymerisation of racemic 3-methylpent-1-ene (IX) and 3,7-dimethyloct-1-ene (X)[54],



(IX)



(X)

where the asymmetric carbon atoms are in the α-position relative to the double bond, on the catalytic system comprising titanium tetrachloride and di[(*S*)-2-methylbutyl]zinc, polymers with considerable optical activity are formed. The optical activity of the polymer fraction increases with increasing molecular weight and melting point of the fraction, i.e. the findings are typical of asymmetric chain growth. When the degree of polymerisation of both monomers (IX) and (X) was between 7 and 22%, the unreacted monomer had appreciable optical activity. The sign of the rotation of the monomer showed that in this case the monomer enantiomorph having the same absolute configuration as the (*S*)-2-methylbutyl groups of the catalytic system was mainly incorporated in the chain. The ratios of the rates of polymerisation of the two enantiomorphs were calculated from the optical activity of the unreacted monomer and the percentage polymerisation of the monomer. It was found that the monomer with the (*S*)-configuration of the asymmetric carbon atom in the side-group polymerises 1.2–1.7 faster than the corresponding (*R*)-monomer.

The sign of the rotation of the polymers is consistent with that predicted on the basis of the absolute configuration of the preferentially polymerised monomer enantiomorph. Thus the considerable differences observed in the polymerisation of racemic 4-methylhex-1-ene, 3-methylpent-1-ene, and 3,7-dimethyloct-1-ene confirm the importance of the effect of the monomer structure on the stereospecificity of polymerisation. It may be concluded that the catalytic system titanium tetrachloride + di[(*S*)-2-methylbutyl]zinc is capable of polymerising electively one enantiomorph of a racemic α-olefin with the asymmetric carbon atom in the α-position relative to the double bond, but the electivity of this catalyst is extremely low when the asymmetric atom is in the β-position.

The stereoelectivity of the catalytic system depends also on the bond between the metal and the optically active group in the organometallic component[45]. Thus in the polymerisation of 3,7-dimethyloct-1-ene appreciable stereoelectivity is observed only with the organozinc compound [the ratio of the rates of polymerisation of the enantiomorphs in the presence of the zinc catalyst is 1.22; in the presence of organoaluminium and organoindium compounds no appreciable differences in the rates of polymerisation of (*R*)- and (*S*)-enantiomorphs are observed]. The author's explanation is that among all the organometallic compounds only the organozinc compound exchanges slowly its alkyl radical for the monomer.

In the study of the crystal structures of the polymers obtained from optically active and racemic α-olefins it was observed that the structures of poly-3-methylpent-1-enes and poly-4-methylhex-1-enes[14] are identical, but the structure of poly-(*S*)-5-methylhept-1-ene[13] is different from that of its racemic analogue. The structural identity of the polymers of (*S*)-4-methylhex-1-ene and the racemic 4-methylhex-1-ene confirms the theoretical prediction that the polymer formed from the racemic monomer is not a random copolymer of the two enantiomorphic monomers but is a mixture of two types of macromolecules. This was demonstrated by the chromatographic separation of the racemic polymer (fraction soluble in ether) on optically active poly-(*S*)-3-methylpent-1-ene[55]. On elution with ether several polymer fractions were isolated, the first having a molar rotation $[M]_D = -17.5°$ and the last being dextrorotatory with $[M]_D = +62.5°$. This study provides one of the most important demonstrations of the stereoselective polymerisation of a racemic monomer. In addition, the possibility of such separation of a polymer implies that in the isotactic growth of each macromolecule stereospecific catalysts can select preferentially one of the enantiomorphic forms of the racemic monomer, even when the asymmetric carbon atom is not directly linked to the double bond of the monomer.

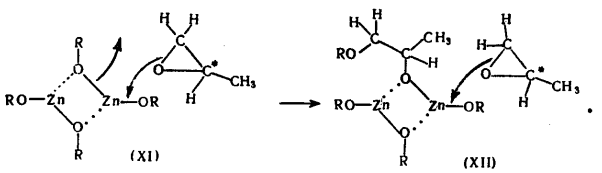
The identity of the crystal structures of the polymers obtained from different enantiomorphs and racemates of propylene oxide[27] and 2-methylbutanal[18] also indicates the stereoselectivity of the polymerisation of these monomers.

This is demonstrated directly by the successful separation of crystalline poly[(±)-propylene oxide][56] on poly[(-)menthyl glycidyl ether] into two fractions with $[\alpha]_D^{15} = -6.7° \pm 1.7°$ and $[\alpha]_D^{15} = +6.4° \pm 1.1°$.

Inoue et al.[57] described the synthesis of optically active poly(propylene oxide) using the racemic monomer and diethylzinc with optically active cocatalysts [(-)-menthol, (-)-borneol]. The optical "purity" of the polymers, determined from the specific rotation, was not more than 20%.

The occurrence of asymmetric induction was confirmed[58] by the isolation from the reaction mixture of the optically active unreacted monomer, the sign of whose rotation was opposite to that of the rotation of the monomer, preferentially incorporated into the polymer chain. It was found that, when (+)-borneol is used as the cocatalyst, L-(+)--propylene oxide is preferentially incorporated into the polymer chain.

Having analysed the optical rotations of the polymer and the unreacted monomer, Inoue et al.[59] concluded that the rotatory power of the polymer formed on the diethylzinc–(+)-borneol system is due to the preferential polymerisation of the L-enantiomorph of propylene oxide. In the initiation step propylene oxide molecules are coordinated to the catalyst, which is a cyclic dimer (XI), and are then incorporated at the site of the rupture of the Zn–O bond[60]. Chain growth proceeds according to the mechanism



(XI) (XII)

When the catalyst does not have asymmetric centres, k_{iL} should be equal to k_{iD} and the reaction should yield a mixture of polymeric molecules with a definite symmetrical distribution of tacticity in which the proportions of the L- and D-monomeric units in the chain range from 100% L to 100% D. If the catalyst contains optically active groups, the rate constant k_{iL} will differ from k_{iD}. For the system diethylzinc–(+)-borneol, $k_{iL} > k_{iD}$ and therefore L-monomeric units predominate in the polymer; also $k_{LL} > k_{LD}$. This example confirms the hypothesis of asymmetric growth.

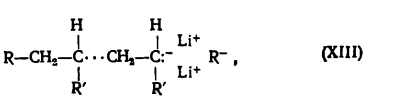
Stereoelective polymerisation of racemic propylene oxide was also achieved by Livshits and Krylov[61] on a heterogeneous stereospecific catalyst — magnesium D-tartrate. Interesting results were obtained by Furukawa and coworkers[62] in the polymerisation of racemic propylene oxide on Pruitt and Baggett's catalyst[63], prepared by the partial hydrolysis of the ferric chloride complex of propylene oxide in the presence of D-bornyl ethyl ether. The unreacted monomer was enriched in the L-enantiomorph of propylene oxide; however, the polymer did not show optical activity although it was a mixture of the crystalline isotactic fraction with a small proportion of amorphous polymer.

Observations of fundamental importance were also made in the study of the adsorption of racemic propylene oxide on an asymmetric catalytic system at a low temperature (under conditions where there is no polymerisation). After being added to the catalyst, the racemic monomer was distilled off in a vacuum. After that triethylamine was added to the residue and the volatile products were again distilled. Measurements of the optical activity showed that the propylene oxide in the first distillate was enriched in the L-monomer and in the second distillate in the D--monomer. Kinetic study of the reaction showed that the observed ratio of the D- and L-enantiomorphs of propylene oxide in the adsorbed monomer is consistent with the ratio of the rates of polymerisation of the enantiomorphs on the given catalytic system. On this basis, it was concluded that the chain growth consists of two stages, adsorption (coordination) and ring opening, and that the inequality of the rates of polymerisation of the enantiomorphs of propylene oxide is mainly due to the difference in the rate of adsorption. However, a final explanation of the lack of optical activity of the polymer was not obtained.

The polymerisation of the *N*-carboxy-anhydride of D- and L-alanine[64] in the presence of a number of asymmetric catalysts [(+)-borneol, (-)-menthol, $Al(C_2H_5)_3$–(+)-borneol, etc.] gave optically active water-soluble polyalanine fractions. Matsuura et al.[65] attempted to carry out the asymmetrically induced copolymerisation of propylene oxide and a cyclic anhydride with an asymmetric carbon atom (the anhydride of 3-phenyl-Δ_4-tetrahydrophthalic acid) on the diethylzinc–(+)-borneol catalytic system. To elucidate the possibility of the asymmetric selection of one or both monomers in the copolymerisation, measurements were made of the optical activity of the unreacted propylene oxide and the anhydride and also the hydrolysis products of the polyester which had regularly alternating propylene glycol–dicarboxylic acid ester units. It was found that the unreacted anhydride (in the form of ester) has positive rotation and the dicarboxylic acid negative rotation, while the unreacted propylene oxide and propylene glycol are optically inactive. The authors suppose that the preferential selection of one of the enantiomorphs of the anhydride is due to the specificity of the catalytic centres to a greater extent than to the "asymmetrising" influence of the preceding propylene oxide unit.

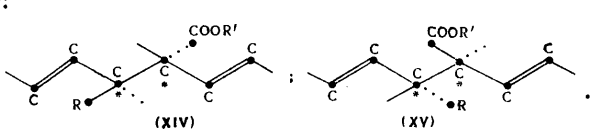
4. Asymmetric Synthesis of Polymers from Monomers without Asymmetric Centres

The preparation of optically active polymers from monomers without asymmetric centres was a considerable advance in the field of asymmetric synthesis. The polymerisation of dienes and monomers of the vinyl and acrylic types can be stereoregulated by using as catalysts lithium or sodium alkyls or aryls in a homogeneous solution. In such cases the end of the growing chain is an ionic quadrupole[66] of the type



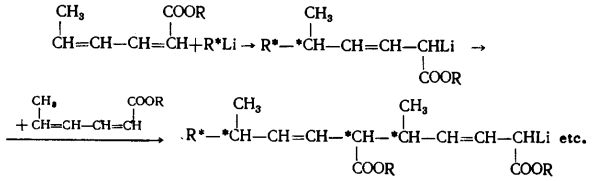
(XIII)

rather than an ion pair. The ionic quadrupole forms a complex with the monomer molecule and controls its incorporation into the growing chain. The polymerisation of dienes substituted in positions 1 and 4, in which on partial dissociation of double bonds two asymmetric carbon atoms arise simultaneously in each unit, was achieved in this way:



(XIV) (XV)

An example is the polymerisation of the esters of sorbic acid and its derivatives and of styrylacrylic acid in the presence of an optically active catalyst — methylbutyl-lithium[67] (Table 2). The polymerisation of sorbic acid esters proceeds according to the following mechanism:



The optically active group of the catalyst plays the role of the "asymmetrising" agent which effects asymmetric induction in the formation of the first asymmetric centre in the chain. Subsequently this function is assumed by the polymer chain whose end forms part of the catalytic complex during the growth process. The catalytic complex ensures the selective incorporation in the chain of units having the 1,4-*trans*-configuration and induces the formation of one of the enantiomorphic forms of the macromolecule.

It must be emphasised that both stereospecific polymerisation and asymmetric synthesis in the presence of anionic homogeneous catalysts are carried out at as low temperatures as possible (between -20° and -80°) at which the number of possible conformations of the monomer molecules is greatly reduced and the monomer–catalyst complexes are more stable. In such cases it is to be expected that the conformation of the terminal groups or of the first monomer unit will influence the configuration of the subsequent monomer units. Reduction of temperature significantly increases the stereospecificity of asymmetric synthesis also in the case of small molecules.

When the polymer was decomposed by oxidative cleavage of the double bond, optically active di- and tri-carboxylic acids were isolated, which means that the optical activity of the polymers is of a configurational type, i.e. it is related to the presence of asymmetric carbon atoms in the main chain. This method makes it possible to determine the optical "purity" of polymers, provided that oxidation is not accompanied by partial racemisation of the acids.

In the presence of racemic lithium alkyls a polymer consisting of a mixture of two enantiomorphic forms is obtained. This polymer is optically inactive.

TABLE 2. Unsaturated esters used as monomers in asymmetric syntheses.

Monomer	Formula of the monomer and the corresponding monomeric unit
Esters of β-vinylacrylic acid (penta-dienoic acid)	$CH_2=CH-CH=CH-COOR$ → $\sim CH_2-CH=CH-\overset{*}{C}H(COOR)-CH_2-CH=CH-\overset{*}{C}H(COOR)\sim$
Esters of sorbic acid (hexa-2,4-dienoic acid)	$CH_3CH=CH-CH=CHCOOR$ → $\sim (CH_3)\overset{*}{C}H-CH=CH-\overset{*}{C}H(COOR)-\overset{*}{C}H(CH_3)-CH=CH-\overset{*}{C}H(COOR)\sim$
Esters of β-styrylacrylic acid (5-phenyl-pentadienoic acid)	$C_6H_5CH=CH-CH=CHCOOR$ → $\sim \overset{*}{C}H(C_6H_5)CH=CH-\overset{*}{C}H(COOR)\cdot\overset{*}{C}H(C_6H_5)\cdot CH=CH\cdot\overset{*}{C}H(COOR)\sim$ (R = methyl and butyl)

A further advance was the use of a cocatalyst as the "asymmetrising" agent instead of the catalyst itself. This was done in the polymerisation of sorbic acid esters in the presence of an inactive catalyst and ethyl (-)-menthyl ether as an optically active additive[68]. This gave an optically active polymer with the same specific rotation as that obtained in the presence of an optically active lithium alkyl.

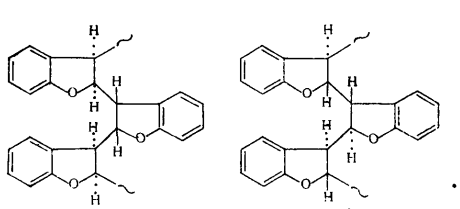
The original studies on the stereospecific polymerisation of *trans*-penta-1,3-diene using an optically active label were carried out by Natta and Porri[69]. This monomer gives rise to two types of crystalline polymer with 1,4--units. The polymerisation of the diolefin in the presence of an organometallic homogeneous catalyst yields a syndiotactic *cis*-1,4-polymer without optical activity as a result of internal compensation, while on a heterogeneous catalyst (based on vanadium trichloride and optically active tri--isopentylaluminium) the product was an optically isotactic *trans*-1,4-polymer.

Systematic study of the optical activity of the polymers obtained under different conditions in the presence of various catalysts can provide useful information about the reaction mechanism and in particular about the structure of the stereoblock-copolymers.

Another study of the same workers and Valenti[70] dealt with the elucidation of the nature of the active centres on heterogeneous Ziegler catalysts. A comparison was made of the capacities of two types of optically active catalysts of the coordination type to induce asymmetry in isotactic poly-*cis*-penta-1,4-diene: (1) (+)-tri-(2-methylbutyl)-aluminium and tetrabutoxytitanium; (2) triethylaluminium and (-)-tetramethoxytitanium. It was found that the polymers obtained in the first catalytic system were optically inactive, while polymers of both low and high molecular weight synthesised in the presence of the second catalyst did show optical activity. Thus asymmetric induction can be explained by supposing that, before being incorporated in the polymer chain, the monomer is coordinated to the organotitanium component whose asymmetric group influences the configuration of the asymmetric carbon atom in the monomer about to be incorporated.

Aliev and Krentsel'[71] achieved the asymmetric polymerisation of *trans*-1-phenylbuta-1,3-diene using two catalysts — (*R*)(+)-2-methylbutyl-lithium and a complex of n-butyl-lithium with (-)-menthylethanol. In the polymerisation with (*R*)(+)-2-methylbutyl-lithium asymmetric initiation took place, while in the presence of the optically active cocatalyst the polymerisation proceeded by the mechanism involving asymmetric chain growth. The degree of asymmetric induction was characterised by the rotational constant *A*, and it was shown that this quantity varies with the method and conditions of polymerisation.

The preparation of optically active polybenzofuran was a considerable advance in the field of asymmetric synthesis of macromolecules[72,73]:



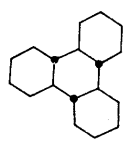
Di-isotactic polybenzofuran was obtained on the cationic catalyst $Al(C_2H_5)Cl_2$ in the presence of optically active co-catalysts: (-)-β-phenylalanine, (+)-β-phenylalanine, (-)-brucine, and others.

The polymerisation of benzofuran involving the opening of the double bond in the heterocyclic ring results in the formation of two possible diastereoisomeric units: *threo*- and *erythro*-di-isotactic units. Since polybenzofuran was not obtained in the crystalline state, the type and conformation of the chain could not be determined. However, the observed optical activity of the polymers indicates the presence of chains or sections of chains having the *erythro*- or *threo*-di-isotactic structure, since only these, among the simplest and most probable structures, would give rise to enantiomorphic chains. In *erythro*- and *threo*-di-isotactic structures all the carbon atoms in the chain are asymmetric and internally non-compensated.

The asymmetric carbon atoms of polybenzofuran exhibit an unusual type of asymmetry and cannot be assigned to the *R* or the *S* type in the nomenclature of Cahn et al.[74], whereby the configuration of the asymmetric carbon atom is established using the rule of the seniority of substituents. Indeed the carbon atom in the polybenzofuran chain in the α-position relative to the oxygen atom is linked to hydrogen, oxygen, and two carbon atoms, which are identical but belong to two different rings. A similar situation obtains also for the β-carbon atom.

To determine the seniority of the apparently identical substituents in the polycyclic compound, Farina and Bressan[75] introduced a new rule, which can be formulated as follows: if two substituents in a polycyclic compound belonging to different rings are identical in accordance with previous rules, the substituent belonging to the same ring as the given asymmetric atom is senior to the substituent linked to the external ring (the *endo*-substituent is senior to the *exo*-substituent).

We may note that a new stereochemical rule is general for polycyclic compounds (both low- and high-molecular) with the above type of asymmetry. For example, the absolute configuration of the isomers of perhydrophenylene[76], which has six asymmetric carbon atoms with a type of asymmetry similar to that found in polybenzofuran, was established on the basis of this rule:



(*R*)-*trans*-*anti*-*trans*-*anti*-*trans*-perhydrophenylene.

Best results were obtained in the asymmetric polymerisation of benzofuran using the system aluminium chloride–(-)-β-phenylalanine (component ratio 3 : 1).[75] During the polymerisation the catalyst, cocatalyst, and the end of the growing chain form part of the catalytic complex which effects asymmetric induction in each fundamental chain-growth step. In contrast to polysorbates, at the end of the reaction the macromolecules do not contain chemically combined components of the catalyst.

The product $[\alpha]n$, where n is the degree of polymerisation and $[\alpha]$ the specific rotation of a single monomeric unit, is proportional to the number of monomeric units, with rotation of a given sign, present in excess. If the hypothesis of asymmetric growth is valid, the relation between $[\alpha]n$ and n should be linear, while in the case of asymmetric initiation the relation should be represented by a curve tending to a limit.

On the other hand the quantity $W[\alpha]$, where W is the total weight of polymer per mole of catalyst, represents the total contribution of asymmetric synthesis in the polymerisation reaction. The study of the variation of $W[\alpha]$ with the amount of initiator in the polymerisation of benzofuran in the presence of aluminium chloride and (+)- and (-)-β-alanine showed that $[\alpha]$ decreases and $W[\alpha]$ tends to a limit, which confirms the hypothesis of asymmetric initiation. However, it is possible that during the polymerisation the counterion is racemised. The mechanism based on this hypothesis can explain both asymmetric growth and the disappearance of asymmetric induction, caused by the alteration in the counterion during the polymerisation process.

Schmitt and Schuerch[77] studied the cationic polymerisation of a number of unsaturated compounds: 4,5-dihydro-2-methylfuran, indene, α-angelica lactone, and cyanocyclopentene in the presence of boron fluoride and different additives, namely (-)-α-methylbenzyl alcohol, toluenesulphonyl-L-valine, and (+)-camphor. The resulting polymers contained asymmetric carbon atoms in the main chain but did not show optical activity. Examination of the molecular models of these polymers showed that in all cases syndiotactic structures are formed, which explains the absence of optical activity.

Thus we see that asymmetric synthesis of macromolecules can be achieved using the same methods of stereoregulation as in the usual stereospecific polymerisation (heterogeneous catalysis with anionic initiation for polyhydrocarbons, ionic initiation in solution at a low temperature for sorbic acid esters, benzofuran, and propylene oxide).

IV. MODIFICATION OF OPTICALLY INACTIVE POLYMERS BY LOW-MOLECULAR OPTICALLY ACTIVE COMPOUNDS

One of the methods for the preparation of optically active polymers is modification of optically inactive polymers by optically active low-molecular compounds. Thus a number of optically active polymeric salts were obtained by allowing optically active acids and bases to act upon optically inactive polyelectrolytes[4,78]. Comparison of two specimens of polyacrylic acid, obtained by the polymerisation of the monomer[79] and the hydrolysis of the anhydride of polyacrylic acid[80], shows that they are completely identical as regards infrared spectroscopic data and the content of carboxy-groups. At the same time the specific rotations of their salts with the optically active alkaloid quinine are different[4]. Probably the difference is due to the different microtactic structures of the initial polyacrylic acids. Thus the optically active label proved to be the most sensitive method for the detection of a difference in the microstructure of a polyelectrolyte.

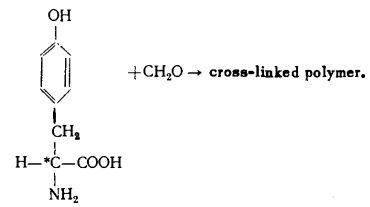
V. PREPARATION OF OPTICALLY ACTIVE POLYMERS BY POLYCONDENSATION

In principle the polycondensation method does not provide a possibility of inducing the formation of new asymmetric centres in monomers — it can only alter the environment of the already existing asymmetric atoms. There

remain two possibilities — one can use optically active monomers (pairs of monomers) or one can carry out asymmetric stereoelective polycondensation during which the optically active component incorporates selectively into the polymer chain one of the enantiomorphs of the other component which is present as a racemate:

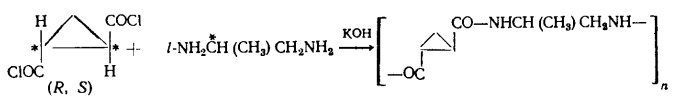
$$R + (R' + S') \rightarrow RR'RR'RR'RR' \ldots\ldots$$
$$\text{or } RS'RS'RS'RS' \ldots\ldots$$

Losse and coworkers[81] obtained an optically active cross-linked polymer by the polycondensation of L-tyrosine with formaldehyde:



This product is insoluble in organic solvents and it is impossible to determine its rotation. It exhibits ion-exchange properties and may be used for the separation of racemates by virtue of its asymmetric carbon atoms. The use of synthetic optically active polymers for the separation of racemates has also been described by other workers[82,84]. Other examples of the synthesis of optically active polymers by polycondensation may be adduced.[85,92] The greatest interest attaches to the synthesis of polycondensation polymers by kinetic racemate separation. Several examples of successful separation of low-molecular racemic compounds by this method are described in the literature. Markwald and Meth[93] described the separation of racemic mandelic acid in the formation of its (-)-menthylamide; Markwald and McKenzie[94] achieved the separation of the same acid in its esterification with (-)-menthol and (-)-borneol.

An attempt to carry out a reaction of a similar type under polycondensation conditions was made for the first time by Topchieva et al.[95], who investigated the system (-)-propylenediamine–racemic *trans*-cyclopropane-1,2-dicarboxylic acid dichloride (containing two asymmetric centres in the molecule). The optically active polymer was synthesised by interfacial polycondensation:



In order to determine whether or not one of the enantiomorphs of *trans*-cyclopropane-1,2-dicarboxylic acid is selected kinetically, a study was made of the optical activity of the acid which failed to undergo polycondensation and the acid isolated after hydrolysis of the polymer. In both cases the optical activity proved to be zero. Control experiments demonstrated that the absence of optical activity in the acid specimens is not due to secondary racemisation processes. Thus it was established that the selection effect does not occur. Application of the usual methods of stereospecific polymerisation, reaction carried out at low temperatures, in the presence of complexing agents, and on the surface of adsorbents, also failed to give the expected results[96]. Probably further advances in the study of such a system (optically active diamine–racemic acid chloride) will involve the study of the microstructure of the polyamide which may throw light on the specific features of this reaction.

VI. OPTICALLY ACTIVE POLYMERS AS CATALYSTS

One of the most interesting applications of optically active polymers is their use as catalysts. Enzymes, which consist of proteins, i.e. optically active polymers of α-amino-acids, constitute a notable example of highly specific catalysts of chemical reactions in living organisms under very mild conditions. The catalysts employed in chemistry are only effective under more severe conditions and show little specificity.

The chemical composition of proteins does not explain this superiority of enzymes over synthetic catalysts. It is known that the groups in the side-chains of proteins (thiol, imidazole, indole, and others) can behave as catalysts in some cases, but their catalytic activity is very low. The problem arises how these groups acquire such exceptional properties when they are incorporated into the composition of a giant protein molecule.

In the attempts to find the answer to this question a number of model reactions using low-molecular compounds as analogues of enzymic systems have been discovered. The mechanisms put forward for these reactions are based on the concepts of electron density and steric hindrance adopted in organic chemistry. Probably, for a more profound understanding of model reactions, it will be of interest to use high-molecular compounds with functional groups, which are closer analogues of enzymes than low-molecular compounds.

In the light of what has been said above, the importance of the new technique based on the use of optically active polymers as catalysts of chemical reactions becomes clear.

Two ways of employing optically active polymers may be distinguished: (1) in the stereospecific catalysis of reactions involving low-molecular compounds; (2) in catalytic stereospecific synthesis of high-molecular compounds. Both these cases are realised in nature with the aid of enzymes and can also be achieved *in vitro*. It is known that enzymes acting upon substrates containing an asymmetric carbon atom usually attack only one of the two enantiomorphs[97]. The specificity of this type is as a rule absolute, i.e. the enzyme is completely incapable of reacting with the other enantiomorph. This notable property of enzymes was used by Pasteur for the separation of racemic mixtures.

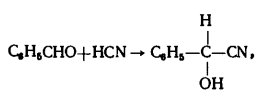
On the other hand, if the substrates consists of symmetrical molecules and the product contains an asymmetric carbon atom, then a symmetric synthesis under the influence of an enzyme results in the formation of only one enantiomorph. Thus the reduction of pyruvate in the presence of L-lactic dehydrogenase gives only L-lactate, while the product of the same reaction catalysed by another dehydrogenase is D-lactate[97].

Apart from the type of stereospecificity mentioned above, there exists yet another, namely the possibility of different behaviour of chemically identical groups in *meso*-compounds. Thus in the reaction

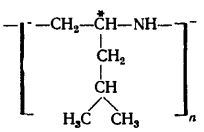
$$Cx_2yz \rightarrow Cx'xyz$$

(where primed letters denote groups attached to the carbon atom) the enzyme may act only on one of the two chemically indistinguishable x-groups. This is proved by the formation of only one enantiomorph of the asymmetric compound $Cx'xyz$. Such specificity has been observed with enzymes of the tricarboxylic acid cycle which are involved in the formation and breakdown of citric acid[98].

The generally accepted treatment of the specificity of enzymes is based on the classical "template" or "key in lock" model proposed by Fischer, Erlich, and others. In this model part of the surface of the enzyme molecule is regarded as a three-dimensional mould of a certain part of the substrate molecule. In other words, the surface of the substrate molecule is from the beginning, before reaction, complementary to the surface of the enzyme molecule. Recently the requirement of steric correspondence, which is a characteristic feature of the "template" hypothesis, has been supplemented by the "flexible" enzyme postulate, i.e. the possibility of inducing changes in the protein structure of the enzyme[99]. At the present time only one study has been made in which a synthetic optically active polymer has been successfully used as a catalyst for the asymmetric synthesis of low-molecular compounds. Tsuboyama[100] studied the synthesis of benzaldehyde cyanohydrin,



in the presence of optically active polyisobutylethyleneimine (PIBI):



The cyanohydrin synthesis involves the nucleophilic addition of the CN^- group to the carbonyl carbon atom and is catalysed by bases. On the one hand, the optically active polymer plays the role of a base which facilitates the dissociation of hydrocyanic acid and, on the other hand, by virtue of the steric effect of the isobutyl group of the polymer adjacent to the amino-group, the transition state is fixed so that the CN^- group can attack the carbonyl oxygen only in a particular direction relative to the isobutyl group.

Compared with other optically active polymeric bases, PIBI ensures the highest yield of an optically active product of the reaction (about 20%). The author concluded that the spiral structure of the polymer has a significant influence on the asymmetric synthesis.

In connection with Tsuboyama's results, it is interesting to investigate the relation between catalytic activity and the conformation of the polymer in solution and its molecular weight. Such data would bring us closer to an understanding of the nature of the "active centre" in a given catalytic system.

Another, more interesting approach involves the asymmetric synthesis of polymers in the presence of already existing optically active polymers. This problem is particularly important, since all natural biopolymers (proteins and nucleic acid) are synthesised in the living organism with the aid of appropriate optically active matrices. The attempts to achieve similar reactions with synthetic polymers have been unsuccessful. Thus in the synthesis of a polymer from racemic propylene oxide in the presence of optically active poly-(L-propylene oxide)[101] the product had a considerable optical activity even at low conversions but the activity was fully accounted for by the optically active seeding material.

Considerable advances in this field have been made by the achievement of enzymic syntheses of nucleic acids *in vitro* in the presence of templates. These include the Kornberg reaction[102] in which DNA has been synthesised on a DNA template in the presence of a universal enzyme (DNA-polymerase) from four monomeric nucleoside triphosphates; the product is a chemical copy of the primer. The catalyst in this reaction is a complex of the enzyme and the template, the former ensuring the formation of phosphodiester links, while the template is responsible for a specific sequence of the nucleosides in the reaction product.

Apart from the synthesis of DNA from all four monomeric units, Kornberg's enzyme gives the copolymer poly(A+T) on addition to a mixture of adenosine and thymidine triphosphates[103]. Without the primer the reaction is initially very slow with an induction period of several hours. After that the polymer formed initially itself serves as a template, i.e. the reaction proceeds autocatalytically. The high-molecular reaction product is a regularly alternating copolymer ATAT...

When Kornberg's enzyme is allowed to act on a mixture of monomers containing guanosine and cytidine only[103], the result is different: the products are equal amounts of the homopolymers polyguanosine and polycytidine, which form double helices by complex formation.

Apart from its template function (replication), DNA is also capable of acting as a primer for chain growth. The lower limit of the length of the primer molecule is equivalent to three nucleosides. The minimum length of the template molecule required for replication is equivalent to about twenty nucleosides. The template and primer functions may be superimposed.

Weiss and Nakamoto[104] discovered a new enzymic reaction involving the replication of RNA on DNA which behaves as a template. Enzymic systems have also been found in which polymeric RNA is synthesised from nucleoside triphosphates on an RNA (and not DNA) template[105].

The non-enzymic syntheses of polysaccharides, polynucleotides, and nucleic acids on templates are of considerable interest[106]. Thus the polymerisation of uridine monophosphate is accelerated by a factor of more than ten in the presence of polyadenylic acid. The introduction of polyarginine also accelerates the synthesis of polyuridylic acid. However, the addition of polyuridylic acid itself does not affect the reaction. The very important conclusion that there exists a mutual relation between the template acting as the catalyst and the monomer follows from

these experiments. Apparently a necessary condition which must be fulfilled in order that the polymer introduced into the reaction behaves as a template is the complementarity of the monomeric unit of the polymer and the monomeric substrate (uridine–adenine).

We shall now consider the problem of the asymmetric synthesis of polymers on templates. In this case complementarity presupposes also a correspondence between the absolute configurations of the asymmetric carbon atoms of the template and the monomeric units of the growing chain. For polymerisation to occur, the polymeric template should possess, in addition to adsorption capacity, the ability to initiate the reaction, and if this condition is not fulfilled a catalyst must be added to the reaction mixture.

The study of the adsorption of polymers from solutions on solid polymers (or association of different types of polymers) may be important for the choice of the polymeric template. Possibly, adsorbability (or capacity for association) may eventually be used as a measure of complementarity.

The problems of the adsorption of polymers on polymers are far from being elucidated. However, it is known that polymers of low molecular weight exhibit highest adsorbability. In addition, it has been observed in the chromatographic separation of isotactic poly-(*R*, *S*)-4-methylhex-1-ene [55] that adsorption interaction occurs between polymers with the same absolute configuration of the asymmetric carbon atoms and not on the principle of quasi-racemate formation.

The results obtained in the polymerisation of benzofuran [107, 108], although without direct bearing on the problem of the template role of polymers, merit attention. Farina et al. found [108] that, when benzofuran is polymerised at relatively low monomer concentrations, the resulting polymer has initially a relatively low optical activity which rapidly increases with the degree of polymerisation to a maximum, and then falls slowly.

The study of the optical activity of polymers synthesised in the presence of previously prepared optically active and inactive polybenzofurans led to the hypothesis of the autocatalytic effect of polybenzofuran on asymmetric synthesis. It is interesting that the autocatalytic effect is independent of both the sign and magnitude of the optical activity of the added polymer. The sign of the optical activity of the polymer synthesised depends only on the sign of the optical activity of the asymmetric initiator employed (the sign of the optical activity of the polymer is the same as that of the optical activity of phenylalanine), while the specific optical activity is very high even at low conversions and virtually identical in many of the cases investigated.

On the basis of their results, the authors claim that autocatalysis must be attributed not to a steric effect but to a chemical effect associated with the presence of the polymer in solution. They believe that, as a result of the presence of oxygen atoms of the ether type, polybenzofuran can behave as a Lewis base in relation to aluminium chloride and can in consequence modify the structure of the conjugate ion.

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The studies on optically active polymers have only begun. The considerable theoretical importance of the problems of the asymmetric synthesis of macromolecules and also the wide variety of the possible uses of an optically active label in the investigation of polymerisation processes undoubtedly merit the attention of investigators in the field of polymer chemistry, and the relevant questions require further development.

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THE MECHANISM OF THE HETEROGENEOUS DEUTERIUM–HYDROGEN EXCHANGE REACTIONS OF CYCLOALKANES

B. S. Gudkov and A. A. Balandin

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I. INTRODUCTION

The study of the deuterium–hydrogen exchange in hydrocarbons began soon after deuterium had become available for use in chemical research[1]. The reason for the interest in these reactions is that they can be used to elucidate the mechanisms of various processes, in the first place of hydrogenation–dehydrogenation reactions, and also the nature of the interaction between hydrocarbon molecules and the surface of a solid catalyst. The existence of a relation between the mechanisms of hydrogenation and isotope-exchange reactions has been pointed out frequently[2-4]. Fairly complete reviews of the catalytic isotope-exchange reactions of hydrocarbons have been given by Anderson[5] and Kemball[6]. In the present review we have attempted to examine the special problem of the deuterium–hydrogen exchange in cycloalkanes, which is extremely important both theoretically and practically.

Studies in this field began with the work of Horrex and Polanyi[7], who, in addition to investigating the exchange between cyclohexane and heavy water in the presence of a platinum catalyst, also observed the interaction of gaseous deuterium with cyclohexane. These workers together with Greenhalgh[8] made a more detailed study of the kinetics of the exchange between cyclohexane and deuterium oxide and gaseous deuterium over platinum deposited on glass fibre, determined the activation energy, and put forward certain hypotheses concerning the reaction mechanism. Farkas and Farkas[9,10] also investigated the exchange between a number of hydrocarbons, including cyclohexane, and deuterium over platinised platinum. Balandin and coworkers observed deuterium exchange with cyclohexane on platinum and on chromium oxide catalysts[11].

However, a distinctive feature of all the above investigations is that only the total amount of deuterium which had undergone exchange was determined. However, the main problem in the elucidation of the reaction mechanism is the determination of the amounts of products with different degrees of substitution, i.e. the distribution, which became possible only after the application of mass-spectrometric methods of analysis[12-14]. A large part of the investigations in this field have been made using evaporated metallic films as catalysts. This is because they have a number of advantages, such as high purity, high activity, and the convenience of working in a high vacuum, which was pointed out by Beeck and coworkers[15,16], who studied in detail the catalytic and adsorption properties of such films. At the same time the preparation of deposited films with reproducible properties involves considerable difficulties[17-23]. The problem of the relation between the catalytic properties of films and massive catalysts is of considerable importance. Burwell et al.[24] found that the deuterium exchange in a number of saturated cyclic hydrocarbons on evaporated palladium films and on the Pd/Al_2O_3 catalyst takes place by the same mechanism. Anderson et al.[17] demonstrated by electron diffraction that in the cases which they investigated the films have the same crystal structure as the massive metal. However, a number of workers adhere to a different view, namely that the properties of film and reduced catalysts are different[25-27]. In particular, differences have been noted between the lattice constants, electronic work functions, and the electrical conductivities of these catalysts[28-30]. These results are consistent with the data of Hightower and Kemball[31], who found that the behaviour of platinum films and deposited platinum catalysts in the reaction between *p*-xylene and deuterium is fundamentally different.

II. DEUTERIUM EXCHANGE IN CYCLOHEXANE, CYCLOPENTANE, AND THEIR DERIVATIVES

1. Reactions on Metallic Catalysts

One of the theories of hydrogen atom exchange with saturated hydrocarbons was developed by Anderson and Kemball[13,14]. Later their ideas were used to explain the reactions in cycloalkenes[32]. According to Anderson and Kemball, the first stage of the exchange is adsorption of the hydrocarbon with formation of a radical adsorbed on one metal atom and a hydrogen atom adsorbed on a second metal atom. On desorption the radical combines with a deuterium atom which had been adsorbed on a neighbouring metal atom and therefore one hydrogen atom in the hydrocarbon is replaced by a deuterium atom (the so-called simple exchange). This involves the preferential formation of monosubstituted products, polysubstituted products being formed when simple exchange is repeated. This type of exchange has a characteristic form of the probability curve for the distribution of the deuterated products, the concentration of those with a high number of deuterium atoms in the molecule falling sharply. This exchange is typical, in the first place, for reactions of methane and hydrocarbons containing isolated methyl groups linked to quaternary carbon atoms, and for reactions of cycloalkanes on oxide catalysts.

In the reactions on metals the so-called multiple exchange is more characteristic of cycloalkanes. In this type of exchange the molecule is initially adsorbed via two carbon atoms. Then one of the C–M bonds (where M is a metal atom) of the "diadsorbed" cycloalkane breaks and the deuterium adsorbed on a neighbouring metal atom adds on. There is a definite probability that the "monoadsorbed" cycloalkane thus formed again undergoes two-point adsorption in a manner such that the C–M bond is formed at the next carbon atom. When this process is continued, the cyclic molecule as it were "rolls" over the surface. The nature of the distribution of the deuterium-exchange products[13] led Anderson and Kemball to the conclusion that

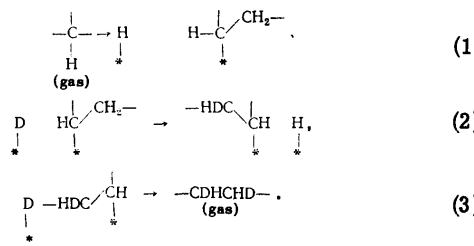
hydrogen atoms can be divided into two groups, those in the first group undergoing exchange more readily than those in the second. In the case of cyclopentane it is quite evident that such groups can only be hydrogen atoms lying on different sides of the plane of the ring. In cyclohexane such classification of hydrogen atoms is not unique but here too examination of the molecular model shows that each group consists of three axial and three equatorial atoms located on one side of the ring (cyclohexane in the "chair" conformation). According to Anderson and Kemball, the exchange of the six hydrogen atoms in the second group is possible only after the molecule turns over on the surface and its opposite side becomes adjacent to the latter. After this, the exchange takes place by the "rolling" method already described. If the possibility of complete desorption of the molecule and its subsequent readsorption via the other side of the ring is disregarded, the turning over of the cyclopentane molecule can only occur via the formation of a second C–M bond, after the rupture of one of these bonds, by a carbon atom already involved in one such bond (adsorption of the $\alpha\alpha$ type[24]). The molecule is then equally likely to lie on the surface on either side. In cyclohexane there is also another possibility — two-point adsorption of the type $\alpha\beta$ in which C–M bonds are formed by two neighbouring equatorial atoms belonging to different groups.

The complex distribution of the products of the deuterium exchange led Anderson and Kemball to the conclusion that two processes can take place simultaneously, one of which is responsible mainly for products with a high deuterium content and the other is responsible for the remaining products. Anderson and Kemball associate these processes with the presence of surfaces having different catalytic activities. On oriented films, where all the crystals are arranged preferentially with the same face directed outward, the distribution is simpler[13].

The model proposed by Anderson and Kemball permits a mathematical calculation of the contents of various deuterium exchange products. However, Hayakawa and Sugiura[33] believe that the hypothesis of the simultaneous occurrence of two processes by no means always leads to agreement between the theoretical and experimental results. Anderson and Kemball suggest that the geometrical disposition of the atoms on the surface is not significant, provided that the distances between the metal atoms lie within a fairly wide range, from 2.4 to 3.1 Å, since any inconsistency between the interatomic distances in the molecule and on the surface is compensated by a change in the C–M distance or slight twisting about the C–C bond. Thus in their view the specificity of metals is not associated with their geometry but with the different contributions of the various adsorption–desorption processes which occur on them. This view does not explain the high specificity of metals in exchange of a particular type. Furthermore, it has been shown that the distribution of the products of the deuterium exchange with cyclohexane on platinum, palladium, and nickel, which have a crystal lattice of the A1 type, is quite different from the distribution in the exchange on tungsten, molybdenum, and iron, which have a lattice of the A2 type[34,35]. The deuterium exchange in cyclohexane on germanium and silicon films is more likely to be of the simple type[36].

Hayakawa and Sugiura[33,37], who studied the deuterium exchange in cyclohexane on evaporated molybdenum and tungsten films, raised a number of objections to the explanation proposed by Anderson and Kemball. They believe that there is no hindrance to the turning over of the molecule and therefore the distribution curve should not exhibit any discontinuities. This was confirmed by their experiments. However, they agree that the exchange involves the rolling of the molecule over the surface. In their view the uniformity of the distribution (i.e. the ease of the transition of the exchange interaction from one side of the ring to the other) ensures firstly two-point adsorption of two equatorial atoms belonging to different groups and secondly the readsorption of the desorbed deuterated products. The second factor can play a significant role only at high extents of reaction, since at low extents of reaction the fraction of molecules which have participated in the exchange twice is $y^2/2$, where y is the total fraction of the molecules which have undergone exchange[6]. However, the high isotope dilution by light hydrogen in their experiments unfortunately limits somewhat the validity of their conclusions. Furthermore, the two catalysts which they investigated are very similar in properties and have a crystal lattice of the same type (A2).

The mechanism proposed by Anderson and Kemball was adopted and developed by Burwell and coworkers[24,38–41], who considered the stereochemical aspect of the reactions. They believe that the exchange takes place via the following stages[38] (the asterisk denotes the catalyst):



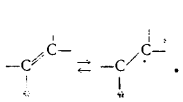
(1)

(2)

(3)

Frequent repetition of stage (2) leads to the formation of highly deuterated products. It is readily seen that this stage is analogous to "rolling" in the mechanism of Anderson and Kemball.

It is known that cyclopentane and hence also the intermediate compound adsorbed at two points may be present in a unique conformation. In this molecule all the hydrogen atoms on one side of the ring lie in pairs in one plane, i.e. they are eclipsed. Thus during the exchange cyclopentane must necessarily form compounds in the eclipsed conformation adsorbed at two points. It has been concluded[24] that, since the mode of distribution and the course of the exchange in cyclohexane and cyclopentane are similar, the intermediates must also be similar and that means that in the case of cyclohexane they are in the eclipsed conformation too. Hence it follows that the "boat" form must be assumed for the adsorbed cyclohexane molecule, since only this conformation gives rise to neighbouring eclipsed hydrogen atoms in cyclohexane. This in fact accounts for the discontinuity in the distribution curve after half the atoms have undergone exchange. Burwell believes[40] that, for the reaction to extend to the other side of the ring, an intermediate compound of the following type must form:



It is readily seen that here a second C–M bond can form on either side of the ring.

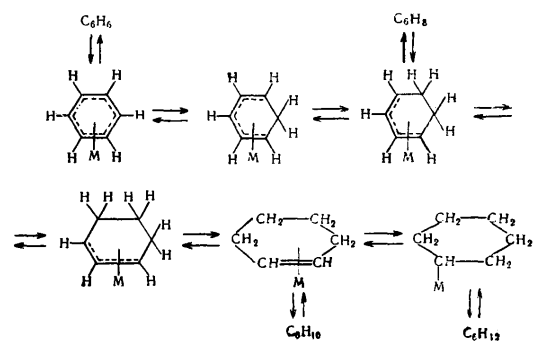
The situation is different in higher cyclic hydrocarbons. Starting with cycloheptane, not only *cis*- but also *trans*--hydrogen atoms may be in the eclipsed conformation, although with some strain in the latter case. In cyclo-octane the formation of the eclipsed conformation in the *trans*--position does not involve any strain. Evidently in such molecules exchange can extend without any hindrance to the other side of the molecule and the distribution curve should not show discontinuities. This view is confirmed by the experimental data of Burwell and coworkers[24]. Whereas the distribution curves for cyclopentane and cyclohexane show distinct peaks corresponding to penta- and hexa-substituted products respectively, in cycloheptane the peak is very small and in cyclo-octane it is virtually absent.

The conclusions of Anderson and Kemball are consistent with the temperature variation of the distribution of the deuterium-exchange products of cyclopentane over palladium found by Burwell et al.[24] They observed a gradual decrease of the maximum corresponding to $C_5H_5D_5$ as the temperature increased from 50° to 170°. Some of their results were obtained for cyclohexane over nickel[38].

The available experimental data demonstrate convincingly the possibility of interpreting the deuterium-exchange mechanism in saturated cyclic hydrocarbons from the standpoint of the multiplet theory of catalysis. Indeed the higher content of hexa-substituted deuteriocyclohexanes in the exchange on metallic catalysts of the platinum group can be explained by models in which the ring lies flat on the surface, in conformity with the sextet mechanism[34,35,42]. The authors of the present review observed[43] that the behaviour of cyclopentane in exchange on metals is quite analogous to that of cyclohexane. The doublet–sextet mechanism, developed by Kazanskii, Liberman, and Plate[44,45], which also requires a planar disposition of the molecule on the surface of the catalyst, was adopted to account for this phenomenon. Thus the higher content of the deuterium--exchange products having the composition $C_nH_nD_n$ can be attributed to the simultaneous exchange of all the hydrogen atoms on the side of the ring turned towards the surface. Evidently, with a planar disposition of the molecule on the surface, cycloalkane molecules with a number of deuterium atoms other than n can also form. This occurs, for example, when the desorption of the cycloalkanes from the surface is rapid, so that the adsorbed molecule has sufficient time to exchange only part of the hydrogen atoms before returning to the space above the adsorbent. Secondary adsorption of partially deuterated molecules can result in the formation of products in which more than half of the hydrogen atoms have been replaced by deuterium. However, the relatively slight excess of molecules having the composition $C_nH_nD_n$ over other exchange products[34,43] suggests that reactions involving two mechanisms, doublet and sextet (or doublet–sextet) take place simultaneously, their superposition yielding the observed distribution[35]. Evidently the sextet mechanism can obtain only on metals which allow a structural correspondence between their crystal lattice and the six-membered ring of the hydrocarbon molecule[42]. Similar hypotheses concerning the superposition of simultaneous processes have been made earlier[13,46]. Anderson and Kemball[13] do not reject the possibility of a doublet mechanism. It is noteworthy that their mechanism and the doublet model of the multiplet theory are not mutually contradictory.

So far we did not concern ourselves with the nature of the bond between the hydrocarbon molecule and the surface of the catalyst. Rooney, Gault, and Kemball[47,48] put forward the hypothesis [and supported it by evidence from experiments on deuterium exchange in various (polymethyl)cycloalkanes on deposited metallic films] that π-complexes are formed as intermediate surface compounds. Essentially the hypothesis is as follows. The usual type of bond between a chemisorbed hydrocarbon molecule and the metal surface is a σ-bond which involves an sp^3-hybridised carbon atom. However, when the molecule contains three or more adjacent non-quaternary carbon atoms there is a possibility of sp^2-hybridisation and delocalisation of p-electrons resulting in the formation of molecular orbitals which arise by the combination of the p-orbitals of the carbon with the unfilled surface d-orbitals of the metal[49]. The energy consumed in the change of hybridisation is compensated by the stability of the bond formed and the delocalisation of π-electrons. Thus the intermediate compound forms a π-bond with the metal similar to that which obtains in ferrocene. As a result of sp^2-hybridisation, the molecule becomes planar and one or other of its two sides turns towards the surface. The metals investigated[48] can be arranged in the following sequence as regards their capacity to form intermediate compounds with π-bonds: Pd > Pt > Ni > Rh.

Developing these ideas, Rooney suggested[50] that during deuterium exchange in cycloalkanes there is a possibility of the formation of three intermediate compounds: initially a σ-bonded alkyl is formed, which is then converted into a π-bonded olefin after the removal of a hydrogen atom (in this process there is $\alpha\beta$-exchange on one side of the plane of the ring), this being followed by the conversion of the olefin into a π-allyl intermediate compound (or a compound with a still more delocalised π-bond). Accordingly, aromatic hydrocarbons and 1,3-dienes are chemisorbed directly as π-bonded complexes. Rooney[50] explained many of the reactions of cyclic hydrocarbons in terms of the mechanism shown below: hydrogenation, dehydrogenation, disproportionation, isotope exchange, and *cis–trans* isomerisation.



Subsequently Rooney emphasised the role of the olefinic π-bond, counterbalanced by the σ-bonds of the intermediate compounds[51]. The problem of intermediate π-complexes in heterogeneous catalysis has been examined in the review of Bond and Wells[52], mainly in connection with unsaturated compounds. The hypothesis of the formation of a planar sp^2-hybridised intermediate compound linked to the surface via a π-bond bears an interesting analogy to the multiplet theory of catalysis, where it is assumed that in the adsorption of cyclohexane on metal catalysts a sextet multiplet complex lying flat on the surface is formed during the dehydrogenation of cyclohexane[42]. Although the molecule forms a π-bond with only one surface atom, this does not

exclude the specificity of the various metals and in particular the effect of geometric factors. The specificity of metals may be due to the relative ease of formation of σ- and π-intermediates. Furthermore, the mode of crystal packing can control the nature of the orbitals in individual metal atoms involved in the formation of the π-bond. In this connection, it may be supposed that the above sextet mechanism of the exchange is associated with the formation of an intermediate π-complex, while the doublet mechanism corresponds to the formation of two σ-bonds with the surface.

This is the general outline of the explanations of the deuterium exchange in cycloalkanes on metals available at the present time. The kinetics of these reactions have been considered to some extent in many of the publications quoted [13,37,38,48]. The kinetic equations obtained are not always the same but they have a certain common feature. Usually the rate of exchange is represented by

$$\omega \propto p_{C_6H_{12}}^{n} \cdot p_{D_2}^{-m},$$

with $n \simeq 1$ and $m = 0.6-1$. Thus deuterium inhibits the exchange [5]. Ravoire [53] made a special examination of the kinetics of deuterium exchange in cyclohexane under static conditions over platinum deposited on activated charcoal, and found that the reaction order and the apparent activation energy can vary on heating above 100°.

2. Reactions on Oxide Catalysts

In the first study of deuterium exchange in cyclic hydrocarbons over chromium oxide [11] it was shown that the reactions on oxide catalysts differ significantly from those on metals. It follows from what has been said above that multiple exchange reactions play a decisive role in deuterium exchange on evaporated metal films. In contrast, on oxide catalysts simple exchange predominates. In this type of exchange each adsorption step involves the exchange of only one hydrogen atom, the molecule being subsequently desorbed, so that species with a low deuterium content are the main products. The activation energy for deuterium exchange on oxide catalysts is as a rule much higher than on metals.

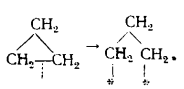
Deuterium exchange in cycloalkanes, mainly cyclohexane, has been investigated on chromium oxide [46,54,55], chromium oxide deposited on alumina [56], and on rare-earth oxides [57-59]. It was shown that the rate of isotope exchange is much higher than the rate of dehydrogenation under comparable conditions [56]. Burwell and coworkers [46] found that, in addition to simple exchange, multiple exchange takes place to a slight extent on chromium oxide (1-2% of the total exchange) and probably also a special type of exchange responsible for the increased content of products with two and three deuterium atoms per molecule. It is suggested that simple exchange involves the interaction between the cycloalkane adsorbed at only one point and a deuterium atom adsorbed at an adjacent site. The hydrocarbon radical may be linked to a chromium atom and the hydrogen to an oxygen atom, the corresponding intermediate product resembling somewhat a carbanion. Burwell attributes the multiple exchange which takes place to a slight extent on chromium oxide to the formation on the surface of an olefin or a π-allyl complex which also incorporates a chromium atom. In view of certain unusual features of the exchange, Burwell and Littlewood [55] suggested that two types of active site are present on the surface of chromium oxide.

Gadzhi-Kasumov, Isagulyants, and ourselves [60,61] arrived at a similar conclusion in a study of the relative extents of deuterium exchange with and dehydrogenation of cyclohexane when the two reactions take place simultaneously on chromium oxide. In these experiments it was found that the degree of dehydrogenation increases steadily with temperature, while the extent of exchange passes through a maximum. It is interesting that, although deuterium exchange in cyclic hydrocarbons is mainly of theoretical interest, it can also acquire some practical value, since this process has been proposed for the enrichment of hydrogen with deuterium [62-64].

III. DEUTERIUM EXCHANGE IN CYCLOPROPANE AND CYCLOBUTANE

Data on the first two, simplest representatives of the cycloalkane series, cyclopropane and cyclobutane, should prove of value for the elucidation of the mechanism of deuterium exchange in these hydrocarbons. Cyclopropane and cyclobutane are somewhat untypical in the series of cyclic hydrocarbons, because of the high Bayer strain in their rings, which reaches 10 kcal per C-C bond in cyclopropane. This excess energy in the molecule can give rise to hydrogenolysis at the same time as deuterium exchange. However, the probability of hydrogenolysis depends to a very great extent on the reaction conditions and primarily on the choice of catalyst. Thus in the reaction of cyclopropane with deuterium in the presence of platinum [65-67], palladium [66,68], rhodium [66,69], and iridium [69] deposited on pumice at temperatures between 0° and 200° cyclopropane is almost completely converted into n-propane. At the same time on an evaporated rhodium film at -100° the exchange and deuterium addition take place at comparable rates [13]; on the other hand, on the chromium oxide catalyst hydrogenolysis becomes appreciable only above 75° and particularly above 100°, while at lower temperatures it does not occur at all [46,54]. The distribution of the exchange products on the chromium oxide catalysts is consistent with the laws of probability — multiple exchange does not take place [54]. In view of the inadequacy of the data for reactions on an evaporated film [13], it is unfortunately impossible to arrive at definite conclusions concerning the mode of distribution. As shown above, under the conditions used for this reaction by Bond and Turkevich [65] and Bond and Addy [66-69], cyclopropane is almost completely decyclised and the main products are n-propanes with 7 and 8 deuterium atoms per molecule.

Since in this case the course of the exchange for cyclopropane and n-propane is almost the same, the reaction mechanisms are probably also identical. Ring opening evidently takes place in the first stage of the adsorption of cyclopropane (this is the rate-limiting stage):



It is noteworthy that under comparable conditions cyclopropane undergoes exchange faster than other cyclic hydrocarbons.

It is apparently more convenient to study deuterium exchange in cyclobutane in view of its greater stability to hydrogenolysis [70]. For example, experiments on the catalytic hydrogenation of ethylcyclobutane showed [71] that the

hydrogenolysis of this compound does not begin until 150°. Despite this, the study of deuterium exchange in cyclobutane itself was undertaken only recently [72]. Until then only derivatives had been investigated — ethylcyclobutane [39,46,54] and 1,1-dimethylcyclobutane [50]. The isotope exchange in ethylcyclobutane on a chromium oxide catalyst at 200–235° yielded a complete set of products containing between 1 and 12 deuterium atoms and also a small amount of products with masses 1–4 units greater than the molecular weight of the fully deuterated ethylcyclobutane [54]. This evidently indicates partial ring opening. The distribution of the deuterium exchange products is consistent with the predominance of simple exchange. Multiple exchange occurs to a comparatively slight extent. In the exchange on an evaporated nickel film partial hydrogenolysis is also observed, but the exchange itself is of the multiple type [39].

It is interesting that in the reaction of 1,1-dimethylcyclobutane on a palladium film only four hydrogen atoms undergo exchange. Rooney [50] attributes this to the fact that for cyclobutane deformation of intermediate $\alpha\beta$-compounds of the olefin type adsorbed on two sites should be hindered, since cyclobutene is less stable than cycloalkanes with larger rings. The formation of an intermediate π-bonded compound of the allyl type is also hindered due to the strain which it must entail in the cyclobutane ring. In the investigation mentioned above, the deuterium exchange with 1,1-dimethylcyclobutane was performed at 68°. An increase of temperature to 150° caused selective cracking to 2,2-dimethylbutane.

Savin and coworkers [72] showed that the reaction of cyclobutane itself with deuterium on evaporated platinum, palladium, nickel, tungsten, and molybdenum films at temperatures between 0° and 171° involves vigorous multiple exchange on all the metals except palladium. It was found that, regardless of the type of the crystal lattice of the metal on which the exchange takes place, the distribution curve for the deuterated products does not show a discontinuity between $C_4H_4D_4$ and $C_4H_3D_5$. This is consistent with the structural postulates of the multiplet theory, according to which there is no structural correspondence between the above metals and the cyclobutane molecule and hence there is no possibility of a process in which initially hydrogen atoms on one side of the ring plane are exchanged and then those on the other side. At the same time, these data contradict the stereochemical hypotheses of Burwell, described above, since according to the latter the distribution curve should have a certain intermediate maximum corresponding to cyclobutane which has undergone exchange to an extent of 50%. It has been pointed out [72] that the exchange in cyclobutane is accompanied by partial hydrogenolysis, which is most intense on nickel. However, this process was slower than the exchange and for short contact times it had relatively little effect on the distribution. Hydrogenolysis was not observed over platinum.

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The study of deuterium–hydrogen exchange constitutes an effective method for determining the mechanism of the interaction between cycloalkanes and the surface of the catalyst. Direct comparison of hydrogenation and deuterium exchange is of particular interest, since it permits a more profound understanding of the mechanisms of these processes. The growing number of studies on these and related problems is clear evidence of the interest which they have for workers in the field of catalysis.

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THE ELECTRONIC FACTOR IN THE KINETICS OF CHEMISORPTION ON SEMICONDUCTORS

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I. REVIEW OF PUBLISHED EXPERIMENTAL WORK

1. Kinetic Laws

The physical and chemical properties of semiconductor surfaces, so important in semiconductor technology and in catalysis, are controlled essentially by chemisorption processes taking place on the surface. For this reason, the study of chemisorption on semiconductors has attracted a great deal of interest.

In order to clarify the fundamental mechanism of chemisorption, it is important to investigate the kinetics of the process. The basic characteristic is the variation of the amount adsorbed q with time t at constant temperature:

the kinetic isotherm $q = q(t)$. Kinetic isotherms are established under two types of experimental conditions: at constant pressure and at constant volume.

Usually, adsorption is fast at the very beginning of the chemisorption process (during the first minute, say), and the kinetics have been inadequately investigated in this region because of the experimental difficulties involved. This stage is followed by a slower one, whose kinetics are usually measured and reported as chemisorption kinetics. However, the chemical interaction between a gas and an adsorbent, whose initial stage is studied in chemisorption, is not confined to this stage. Chemisorption, particularly at high temperatures, can be followed by processes which affect the bulk of the adsorbent: e.g. penetration of adsorbed species into the bulk of the adsorbent, diffusion of metal in stoichiometric excess (in the case of oxide or sulphide semiconductors) from the bulk phase to the surface. In the chemisorption of oxygen on oxides this process is equivalent to growth of the crystal lattice of the adsorbent. Thus, it is important to distinguish, in experimental studies of chemisorption, between chemisorption proper and subsequent stages of sorption. This has not always been done.

The kinetics of the majority of chemisorption processes are described by the Roginskii–Zel'dovich equation[1,2]

$$dq/dt = a\exp(-\alpha q), \tag{1a}$$

where a and α are constants ($a > 0$, $\alpha > 0$). In its integrated form the equation is

$$q(t) = (1/\alpha)\ln(1 + t/t_0), \tag{1b}$$

where $t_0 = 1/a\alpha$.

Eqn. (1) was used by Roginskii and Zel'dovich[3] to describe the kinetics of the chemisorption of CO on MnO_2. Taylor and Thon[4] showed that the equation could be applied to a large number of experimental results. The constants a and α are determined as follows. One chooses a value of t_0 such that the plot of q against $\ln(1 + t/t_0)$ is linear, and from the slope of this plot α is obtained. Knowing α and t_0, we can then arrive at the value of a. We can see from Eqn. (1a) that a corresponds to the initial rate of adsorption: $a = (dq/dt)_{t=0}$. However, if we determine the initial rate of adsorption from the amount of material adsorbed during the first unit of time (i.e. as rapidly as possible after the onset of adsorption), we obtain a value much greater than a found from Eqn. (1b). This is evidence for the existence of a fast initial stage of chemisorption.

The constants a and α depend on T and P as follows: (1) on raising T, α decreases, but a, on the other hand, increases with an activation energy of about 10 kcal mole^{-1}; (2) at constant T, α tends to increase slightly as P decreases, and a increases approximately as $P^{0.8}$. Taylor and Thon conclude that in the slow stage of chemisorption described by Eqn. (1) the kinetics are relatively insensitive to the mass-action effect of the gas, and are determined mainly by changes taking place in the adsorbent.

The Table, reproduced from Stone's book, illustrates the application of Eqn. (1) to chemisorption processes, but does not claim to be comprehensive.

It should be noted that Eqn. (1) formally describes any process in which the height of the potential barrier opposing a change in some quantity is linearly related to the change in that quantity. Thus Eqn. (1) could describe not only the chemisorption stage but also any subsequent absorption stage, although it does not follow that in a kinetic isotherm consisting of two intersecting Roginskii–Zel'dovich straight lines of different slope the second line necessarily denotes some process other than chemisorption.

TABLE. Chemisorption processes conforming to the Roginskii–Zel'dovich equation.

Gas	Adsorbent	Gas	Adsorbent
H_2	Cr_2O_3	CO	MnO_2
	$ZnO\cdot Cr_2O_3$		NiO
	$\alpha MnO\cdot Cr_2O_3$	O_2	$CaO\cdot Cr_2O_3$
	ZnO		NiO
	NiO		CoO

Chemisorption involving the adsorption of more than one layer, and conforming to Eqn. (1), has been observed[5-7] in the adsorption of oxygen on thin films of oxides deposited on the appropriate metal. Engell and Hauffe[8] quote an example of the penetration of oxygen into the NiO lattice, conforming to Eqn. (1), after a chemisorption stage described by the same equation but with a different slope. Parravano and Boudart have pointed out[9] that processes such as bulk and surface diffusion can also follow a logarithmic law. It follows that a wide variety of mechanisms of gas absorption can remain concealed in Eqn. (1).

Although many chemisorption processes are described by the Roginskii–Zel'dovich equation, cases are known in which chemisorption proceeds according to some other kinetic law. Thus, Enikeev and coworkers[10-13] have shown that, when the electron work function of the adsorbent is logarithmically related to the coverage of the surface, a power law is obtained:

$$dq/dt = aq^b, \tag{2a}$$

where a and b are constants ($a > 0$, $b > 0$), or alternatively

$$q(t) = a't^{b'}. \tag{2b}$$

Examples of this behaviour include O_2 on NiO, C_3H_7OH on ZnO, and O_2 on ZnO containing Li_2O. Eqn. (2b) is called the Bangham equation, and has been used by Bangham and coworkers[14,15] to describe the adsorption kinetics of CO_2 and NH_3 on glass.

Thuillier[16] observed, in his study of the chemisorption of oxygen on ZnO, a rate process conforming to the equation

$$dq/dt = a\exp(-\alpha q^2) \tag{3}$$

(a and α constant), which had been put forward by Aigrain and Dugas[17] and Germain[18]. According to Roland and Schuttler[19], Eqn. (3) also describes the kinetics of oxygen chemisorption on TiO_2 (rutile).

2. Reversibility and Irreversibility of Adsorption

Even the earliest studies of chemisorption had revealed the existence of different forms of the bond between the chemisorbate and the surface of the adsorbent. It was found that the whole adsorbate could not always be removed completely from the surface if desorption was carried out at the same temperature as adsorption. Higher desorption temperatures increase the amount of adsorbate removed from the surface, but occasionally the species which is desorbed beyond a certain temperature is not the same as

that which had been adsorbed. This was observed by Garner and Kingman[20,21] during their study of the adsorption of hydrogen and carbon monoxide on $ZnO.Cr_2O_3$. These workers concluded that two types of adsorption are possible on oxides: "reversible" adsorption, when the adsorbate can be desorbed in its original chemical form, and "irreversible" adsorption, when the opposite is true. However, the measured heats of adsorption, which were found to lie in the range of 10–30 kcal $mole^{-1}$, show that even in the case of "reversible" chemisorption we are dealing with chemical rather than physical adsorption.

The presence of two forms of chemisorption was later demonstrated by many workers. The two forms are often termed the weak and the strong form of chemisorption. The relative amounts of the two forms under comparable conditions depend on the temperature at which adsorption is allowed to proceed. Thus, hydrogen adsorbed on zinc oxide below 100° is readily desorbed, whereas at temperatures higher than 100° strong adsorption is observed[22]. The adsorption of hydrogen on ZnO was studied also by Keier and Roginskii[23,24], who found that above 100° an appreciable fraction of the hydrogen is strongly adsorbed and can only be removed from the surface in the form of water by heating the specimen above 500°. The adsorption of carbon monoxide on ZnO shows similar features: several workers[25-27] found that CO which has been adsorbed at room temperature can be desorbed unchanged, whereas above 150° the adsorption is irreversible. A weak adsorption of oxygen on ZnO at room temperature was reported by Putseiko and Terenin[28] and Enikeev et al.[10]; Keier[29] demonstrated the presence of "weak" adsorption at temperatures between 20° and 100°, and "strong" adsorption above 100°. The different forms of chemisorption of oxygen on zinc oxide were investigated also by Barry and Stone[30,31], who concluded that the predominant chemisorbed species at room temperature is O^- whereas above 300° the predominant form is O^{2-}, "stabilised by the diffusion of interstitial zinc towards the surface". The chemisorption of both unsaturated (ethylene, propene) and saturated (propane) hydrocarbons on metal oxides was investigated by Margolis[32]. A definite fraction of the adsorbed hydrocarbon (not more than 10%) is strongly bound to the surface, and can be removed only by baking in oxygen.

The ratio between the weak and the strong form of chemisorption is affected not only by temperature but also by the nature of the adsorbed gas and of the adsorbent. Thus, according to Keier and Kutseva[33] the amount of strongly bound CO_2 on nickel oxide (NiO) is no more than 2.5–3% of a monolayer, whereas oxygen and acetylene are strongly adsorbed, and can only be desorbed from the surface in negligibly small amounts.

Not surprisingly, the difference between the two forms of chemisorption springs from differences in heat of adsorption. Garner and coworkers showed[34] that the fraction of CO and H_2 which is reversibly adsorbed at room temperature varies from oxide to oxide. Thus, CO adsorption on ZnO at room temperature is completely reversible. The heats of adsorption vary between 12 and 20 kcal $mole^{-1}$. On other oxides, such as Mn_2O_3 and $Mn_2O_3.Cr_2O_3$, the heats of adsorption are higher and the chemisorption is irreversible.

Margolis showed[32] that, by introducing various amounts of impurity into the adsorbent, both the adsorption capacity and the ratio between the strong and the weak form of chemisorption can be controlled. Thus, in the adsorption of propene on magnesium chromite ($MgO.Cr_2O_3$) the proportion of the strong form is as follows: 3% in the absence of additives, 10% in the presence of 1% of added Na_2SiO_3, 25% in the presence of 2% Na_2SiO_3, and 50% of the total adsorption in the presence of 3% Na_2SiO_3.

It should be noted that any reference to two forms of chemisorption underlines the existence of different types of bond between the chemisorbed species and the surface. A more detailed study of these forms may reveal the presence of yet more types of bond.

3. Change in Electrical Conductivity and Work Function of the Adsorbent During Adsorption

The strong and the weak form of chemisorption differ in their effect on the electrical conductivity σ of the adsorbent. According to Morrison[35] and Kubokawa and Toyama[36], the weak adsorption of H_2 on ZnO, which takes place below 100°, has no effect on the electrical conductivity, whereas the strong, high-temperature adsorption increases the conductivity. The temperature beyond which adsorption begins to have an effect on σ depends on the method of preparation of the adsorbent. The activation energy for high-temperature adsorption is about twice as large as the activation energy for low-temperature adsorption. The effects on σ of the weak and the strong hydrogen chemisorption on nickel oxide are qualitatively similar to the above[37,38].

Keier's results[29] on the adsorption of ethanol on ZnO are very interesting: adsorption proceeds almost instantaneously at room temperature, and a coverage of 80–85% of a monolayer is obtained in 15–45 s. The conductivity of the adsorbent (pressed discs of ZnO) does not change during adsorption up to a complete monolayer; only after 20 min, when adsorption has gone to completion, does σ begin to increase. The increase then continues for a very long time. At 100° the adsorption of ethanol produces changes in σ two orders of magnitude higher than at 20°. The greater part of the adsorbed alcohol can be removed from the surface by heating at 450°: under these conditions ~ 50% of a monolayer is desorbed unchanged, whilst the remainder undergoes changes and emerges from the surface as CO_2 (and in part as ethylene).

The variation of the work function φ with surface coverage has been examined by Enikeev and others[10-13]. It was found that the sign of the surface charge is determined essentially by the nature of the adsorbed molecule. Changes in work function (for different gases on different semiconductors) span a fairly wide range of values: from tens of millielectron-volts to 0.7–0.9 eV. In some cases these changes are reversible, in others they are irreversible and slow to develop. The adsorption capacity, and also the dependence of φ on coverage, are related to the type of chemisorption: as a rule, the extent of adsorption of a gas is lower for exhaustive (or depletive) chemisorption than for enrichment (or cumulative) chemisorption. In the former case coverages seldom exceed 1–10% of a monolayer, and φ varies linearly with coverage. In the latter case the ultimate coverage can approach a monolayer (O_2 on NiO, C_3H_7OH on ZnO), but φ varies logarithmically with coverage.

It should be noted that a change in φ as a result of adsorption does not necessarily prove that the adsorption is chemical in character. Physical adsorption of dipolar molecules with a large enough dipole can also produce a sizeable change in φ. Such appears to be the case[10] in the adsorption of isopropyl alcohol (C_3H_7OH) on zinc oxide at 20°.

If the dipole moment of the adsorbed molecules is small, the change in φ is a measure of the bending of the energy bands at the surface of the semiconductor, and therefore also of the potential difference between the surface and the bulk. In some cases it has been shown[11] that the change in work function ($\Delta\varphi$) is equal to the change in activation energy for chemisorption (ΔE).

Simultaneous observations of the adsorption kinetics and of the kinetics of the resulting changes in the electronic properties of the semiconductor adsorbent are particularly interesting. Unfortunately, very few investigations of this type have been reported. The kinetics of changes in σ following oxygen adsorption on thin layers of oxides have been examined in a series of papers by Gray, Garner, and their coworkers[37,39], but the experiments did not include simultaneous adsorption measurements. The extent of adsorption was inferred by an indirect method: by assuming that the conductivity was proportional to the square root of the coverage.

Litovchenko and coworkers[40] arrived at the following conclusion from their study of time-changes in φ accompanying the adsorption of oxygen on germanium: "immediately after adsorption the work function φ does not change, i.e. the adsorbed molecules attach themselves to the surface in an effectively neutral state, and gradually undergo charge transfer, which in turn modifies the bending of the bands at the surface".

Enikeev has made a detailed study of the kinetics of changes in φ in conjunction with the kinetics of oxygen chemisorption on manganese dioxide[12,41]. He identifies three stages in the take-up of oxygen: the first stage consists in almost instantaneous adsorption, proceeding without activation energy. Surface coverages are very low (up to 10^{11} cm^{-2}), and the work function increases sharply by 0.20–0.25 eV. The second, and relatively slow, stage is described by the logarithmic Roginskii–Zel'dovich isotherm, Eqn. (1), both as regards coverage and work function. The latter increases linearly with the coverage, which can reach $3-6 \times 10^{12}$ cm^{-2}. Above 100° a new mechanism involving absorption of oxygen by the lattice can be observed. This gives rise to the third and slowest stage. The increase in work function during this stage is minimal.

To conclude this section on experimental studies of the kinetics of chemisorption, we must point out that, in spite of the large number of published papers (see, for example, the review article by Low[2]), very few of these have dealt with simultaneous observations of the rate of gas absorption and of kinetics of changes in the electronic characteristics of the adsorbent (such as the electron work function or the electrical conductivity). Yet, only by combining simple adsorption measurements with electronic measurements can we hope to characterise unambiguously chemisorption phenomena.

II. REVIEW OF THEORETICAL WORK

1. Difference in Approach Between the Boundary Layer Theory and the Electronic Theory of Chemisorption

The origin of the electronic theory of chemisorption on semiconductors goes back to 1947 (F. F. Vol'kenshtein). The results obtained by Vol'kenshtein and his coworkers have been published as a monograph[42]. In 1952 the electronic aspects of chemisorption on semiconductors began to attract attention in many countries: Hauffe and coworkers in West Germany, Weisz in the USA, Germain in France, etc. This work is known under the name of boundary layer theory (Randschichttheorie der Adsorption). It should be noted that until recently the kinetics of chemisorption have been practically ignored in the context of the electronic theory, most of the work being confined to equilibrium aspects of the adsorption problem.

Before proceeding to a discussion of specific contributions to the boundary layer theory (in so far as they relate to the kinetics of chemisorption), we shall dwell upon some characteristic features of the approach of the boundary layer theory to chemisorption problems in general and to the kinetic aspects in particular[8,18,43–48].

Firstly, according to the boundary layer theory a localised surface level within the forbidden gap of the semiconductor (corresponding) to a chemisorbed species) exists only in so far as it is occupied (by an electron in the case of an acceptor level or by a hole in the case of a donor level). In other words, transition to the chemically adsorbed state does not give rise to a level which, as commonly understood, can be either occupied or empty: the resulting level is by definition occupied. The localised surface levels used in the boundary layer theory to represent chemisorbed species cannot be unoccupied. Hence, during adsorption the rate of appearance of chemisorbed species can be identified with the rate of capture of electrons (or holes) by the surface levels rather than with the rate of appearance of these levels: as many chemisorbed particles appear in unit time as there are levels which can become occupied during the same time. Similarly, during desorption the rate of disappearance of chemisorbed species from the surface is identified with the rate at which electrons (or holes) can be set free from the corresponding levels.

In contrast, we note that in the electronic theory[42] the chemisorption of a species generates a localised surface level in the forbidden gap of the semiconductor which can be either free or occupied. In the former case the chemisorbed particle is in the state termed a "weak" bond; in the latter case, when a free electron (or hole) of the semiconductor becomes localised in the level, the bond between the species and the lattice of the adsorbent is stronger and the chemisorbed species is in the state termed a "strong" bond. The relative numbers of the two states (or of the two types of bond) are determined, for a given position of the surface chemisorption level, by the position of the Fermi level at the surface. The chemisorption level will be occupied by an electron (or hole) with practically unit probability only if it is located sufficiently far below or above the surface Fermi level (depending on whether we are dealing with an acceptor level or a donor level). In this case the treatment is formally the same as that of the boundary layer theory (for problems of adsorption equilibrium).

Secondly, most of the work on the boundary layer theory assumes that physical adsorption is invariably involved as a first stage necessarily preceding chemisorption. The physically adsorbed state undergoes a transition to a state in which the species is chemisorbed. The idea of physical adsorption in the boundary layer theory effectively takes the place of the idea of a "weak" form of chemisorption on which the electronic theory relies. We should also note that, as Vol'kenshtein[42] points out on p. 19 of his monograph, the electronic state leading to physical adsorption cannot produce chemical adsorption, and vice versa, so

that transition from physical to chemical adsorption necessarily involves transition of the system to a different electronic state.

One of Hauffe's papers[44] discusses a scheme in which chemisorption (of acceptor species) occurs in the absence of a physical adsorption stage: species are chemisorbed from the gas phase on to surface traps ready to receive an electron and produced by some mechanism other than adsorption. These traps are represented by some localised level in the forbidden gap. Unoccupied traps of this type take part in the act of chemisorption with the status of reactants: their concentration appears as one of the factors in the expression for the rate of adsorption. The act of chemisorption itself is, so to speak, trimolecular: it involves an unoccupied surface trap, a gas species, and an electron from the adsorbent, which is captured from the valence band if the adsorption takes place on a p-type semiconductor or from the conduction band in the case of adsorption on an n-type semiconductor. The nature of the traps is left vague: "they can have various physicochemical origins: for example, they can be physically adsorbed species". We would make the following comment on the statement that physically adsorbed species can generate localised levels in the forbidden gap of a semiconductor. It is well known[42] that the effect of physically adsorbed species on the energy spectrum of the electrons in the adsorbent is confined to a small perturbation. Hence, if such species generate localised levels they must be fairly shallow ones[49].

Hauffe's statement appears to be logical, because it ignores the "weak" bond: this is characteristic of all papers on the boundary layer theory. In fact, if the "weak" bond is effectively absent, we have two alternatives Either we operate with adsorption levels which exist only in so far as they are occupied by electrons (for the case of acceptor species), which "makes nonsense of the very concept of a localised level as a level free to accept or emit electrons",[42] or else we ascribe to physically adsorbed species the property of always generating localised levels whose occupancy is treated as a transition to the state of chemical adsorption, which can hardly be correct.

In view of the different approaches of the boundary layer and of the electronic theory of chemisorption, and also because recent papers within the scope of the electronic theory and dealing with kinetics are not mentioned in Vol'kenshtein's book[42], we shall discuss these papers separately in Section III of the present review.

2. The Boundary Layer Theory

The chemisorption of an acceptor gas was treated by Hauffe as follows[44]. (We shall use, however, the terminology adopted in the electronic theory)[42].

(a) Chemisorption on a p-type semiconductor is a reaction involving a species A from the gas phase and a surface trap B not occupied by an electron. The species A, on becoming adsorbed in the empty trap, "emits a hole into the valence band" (in Hauffe's words):

$$A+BL \rightarrow ABeL+pL,$$

where L denotes the lattice, and eL and pL are an electron and a hole in the lattice respectively. The reverse reaction gives rise to desorption. The energy relationships are summarised in Fig. 1, where B is the trapping level, AB the level of the adsorbed species, FF the Fermi level,

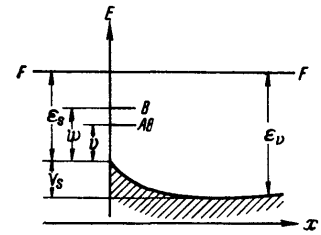

Fig. 1.

and w and v are the distances from the edge of the valence band to the trap level and to the level of the adsorbed species respectively. The overall rate of chemisorption is expressed in the form

$$dN_A/dt = k_1 P N_B (1-\eta_B)\alpha - K_2 N_A p_s.$$

Here N_A is the surface concentration of chemisorbed A species, P the pressure of adsorbed gas, N_B the surface concentration of traps, $(1 - \eta_B)$ the probability of the trap being empty, α the probability of thermal emission of a hole from the species A into the valence band, and p_S the concentration of holes just below the surface.

The following expressions are inserted for $1 - \eta_B$, p_s, and α:

$$\begin{cases} 1-\eta_B = \left(1+\exp\left[\frac{\varepsilon_s - w}{kT}\right)\right]^{-1} & (4a) \\ p_s = C_p \exp\left(-\frac{\varepsilon_s}{kT}\right), & (4b) \\ \alpha = \alpha_0 \exp\left(-\frac{v}{kT}\right), & (4c) \end{cases}$$

whence

$$\frac{dN_A}{dt} = k_1\alpha_0 \exp\left(-\frac{v}{kT}\right)\cdot\left[1+\exp\left(\frac{\varepsilon_s - w}{kT}\right)\right]^{-1}\cdot N_B P - k_2 C_p \exp\left(-\frac{\varepsilon_s}{kT}\right)\cdot N_A. \quad (5)$$

By letting dN_A/dt vanish, it is possible to determine the amount adsorbed at equilibrium; the kinetic equation (5) itself cannot be solved. At the beginning of chemisorption, when the rate of desorption is small, we can ignore the second term on the right-hand side of Eqn. (5).

If

$$\exp\left(\frac{\varepsilon_s - w}{kT}\right) \gg 1,$$

i.e. $1 - \eta_B \ll 1$, or in other words if the surface traps which play the part of adsorption centres are almost fully occupied by electrons, we obtain the following expression for the initial rate of adsorption:

$$\frac{dN_A}{dt} = k_1\alpha_0 N_B P \exp\left[-\frac{\varepsilon_s - (w-v)}{kT}\right].$$

It is not easy to see why chemisorption should require a collision between an impinging particle (species) and an

empty trap with simultaneous capture of a valence band electron by the trap, and why a collision between a particle from the gas phase and a trap already occupied by an electron (i.e. a trap in which an electron had previously become localised) should not be accompanied by chemisorption.

(b) Chemisorption on an n-type semiconductor is treated as a reaction between an empty surface trap BL, a species from the gas phase A, and a free electron from the conduction band eL:

$$A + BL + eL \rightarrow ABeL.$$

Desorption is described by the reverse reaction. The energy relationships are shown in Fig. 2, where w and v now denote the distances from the bottom of the conduction band to the trap level and to the level of the adsorbed species respectively. The equation for the net rate of chemisorption is given in the form

$$\frac{dN_A}{dt} = k_1 P N_B (1 - \eta_B) n_s - k_2 N_A \beta,$$

where

$$1 - \eta_B = \left[1 + \exp\left(\frac{w - \varepsilon_s}{kT}\right)\right]^{-1}, \quad (6a)$$

$$n_s = C_n \exp\left(-\frac{\varepsilon_s}{kT}\right). \quad (6b)$$

$$\beta = \beta_0 \exp\left(-\frac{v - w}{kT}\right). \quad (6c)$$

Here n_S is the concentration of free electrons just below the surface. Hauffe also assumes that

$$k_1 = k_0 \exp\frac{w}{kT}. \quad (6d)$$

The discussion then follows the same lines as for the case of chemisorption on a p-type semiconductor.

We should note that formula (6d) is equivalent to assuming that the rate of filling of the surface traps by electrons from the conduction band increases exponentially with their depth below the conduction band, a hypothesis which is in no way substantiated. Expression (6c), on the other hand, stated that, when a chemisorbed species is desorbed, the electron which was captured by this species is released to an adsorption centre (trap) and not to the conduction band.

Again, it is not clear why a three-body collision should be a prerequisite of chemisorption (impinging gas particle + + empty trap + free lattice electron), and why chemisorption cannot occur at a trap already filled by an electron.

In the discussion of the chemisorption of CO and H_2 on NiO (a p-type semiconductor), the first stage is assumed to be physical adsorption[45]:

$$CO + L \rightarrow CO \cdot L, \quad (7a)$$

where CO·L denotes a physically adsorbed molecule of CO.

The second stage is the transition from the physically adsorbed to the chemisorbed state:

$$CO \cdot L + pL \rightarrow COpL, \quad (7b)$$

where pL is a hole and COpL is a chemisorbed, positively charged CO molecule.

The rate of the first stage (7a) is given as

$$\frac{dN^0_{CO}}{dt} = k_1 P_{CO} - k_1' N^0_{CO} - k_2 N^0_{CO} p_s + k_2' N^+_{CO} \gamma.$$

Here N^0_{CO} and N^+_{CO} denote the surface concentrations of physically and chemically adsorbed CO molecules respectively, P_{CO} is the partial pressure of CO, and p_S the concentration of holes in the layer just below the surface.

The rate of the second stage (7b) is expressed in the form

$$\frac{dN^0_{CO}}{dt} = k_2 N^0_{CO} p_s - k_2' N^+_{CO} \gamma, \quad (8)$$

where (see Fig. 3)

$$p_s = C_p \exp\left(-\frac{\varepsilon_s}{kT}\right),$$

$$\gamma = \gamma_0 \exp\left(-\frac{v}{kT}\right).$$

Assuming that equilibrium between the physically adsorbed molecules and the gas phase is maintained at all times, Eqn. (8) takes the form

$$\frac{dN^+_{CO}}{dt} = k_3 P_{CO} \exp\left(-\frac{\varepsilon_s}{kT}\right) - k_3' N^+_{CO} \exp\left(-\frac{v}{kT}\right). \quad (9)$$

Eqn. (9) cannot be solved. From the condition $dN^+_{CO}/dt = 0$, we find the concentration of chemisorbed CO molecules corresponding to adsorption equilibrium.

Thus, Hauffe's work has been aimed at obtaining adsorption isotherms from the kinetic equations which were formulated, and not at solving these equations in order to characterise the kinetics of chemisorption. We must also point out that according to Hauffe the adsorption level undergoes charge transfer with the conduction band only in the

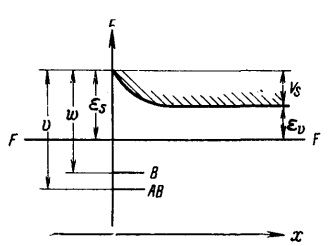

Fig. 2.

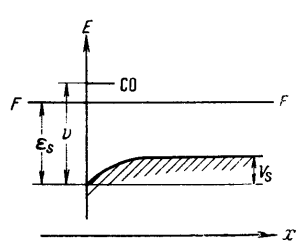

Fig. 3.

case of an n-type semiconductor and with the valence band only in the case of a p-type semiconductor. This implies that the adsorption level must be located near the conduction band for an n-type semiconductor and near the valence band for a p-type semiconductor. This hypothesis is groundless, since the position of the adsorption level in the energy spectrum depends on the nature of the chemisorbed species and on the nature of the lattice, but certainly not on the conductivity type of the semiconductor.

3. Kinetic Model of Chemisorption

Germain has discussed[18,46] what he calls a kinetic model of chemisorption. A molecule held on the surface by van der Waals forces is assumed[18] to give rise to a localised level A in the forbidden gap of the semiconductor (see Fig. 4). For concreteness, the level is assumed to be of the acceptor type. Partly ionised donors are present on the surface (level D):

$$DL \rightleftarrows DpL + eL. \qquad (10a)$$

An electron, donated by the surface donor to the conduction band, is captured from this band by the adsorption level A. As a result, the physically adsorbed A molecule is converted into an A^- ion and passes into the chemisorbed state:

$$A \cdot L + eL \rightarrow AeL. \qquad (10b)$$

Thus, chemisorption results from the consecutive transitions (10a) and (10b), and can be visualised as

$$DL + A \cdot L \rightarrow DpL + AeL. \qquad (10c)$$

It is assumed that the rate of chemisorption is equal to the rate of ionisation of the surface donors D, whose activation energy is taken to be equal to $\varphi - \chi$. The rate of adsorption is expressed in the form

$$\frac{dN_A^-}{dt} = k_1 P_A \exp\left(-\frac{\varphi - \chi}{kT}\right), \qquad (11)$$

where P_A is the pressure of the gas being adsorbed and N_A^- the surface concentration of chemisorbed species (i.e. of A^- ions), with $\varphi = \varphi(N_A^-)$. The rate of desorption is equated to the rate of the reverse reaction (10b), and is written in the form

$$-\frac{dN_A^-}{dt} = k_2 N_A^- \exp\left(-\frac{v - \chi}{kT}\right).$$

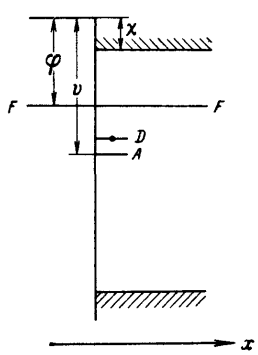

Fig. 4.

(It is evident from Fig. 4 that the difference $v - \chi$ is equal to the depth of the adsorption level below the conduction band.)

The condition of equal rates of adsorption and desorption defines the adsorption isotherm in an implicit form. At the beginning of the chemisorption process the rate is given by Eqn. (11). For small values of N_A^-, it is assumed that

$$\varphi = \varphi_0 + a(N_A^-)^2,$$

so that, taking (12) into account, Eqn. (11) becomes

$$\frac{dN_A^-}{dt} = C \exp[-a(N_A^-)^2],$$

where C and a are constants ($C > 0$, $a > 0$).

However, if a positively ionised surface donor D^+ appears on the surface for every newly produced, negative, chemisorbed A^- ion [see Eqn. (10c)], the surface charge (and therefore also the value of φ) should stay constant during chemisorption, which is of course not the case.

In Germain's[46] work the rate of adsorption is not related to the rate of ionisation of a surface impurity, but is assumed proportional to the pressure (which is taken to be constant) and, for chemisorption of the acceptor type, to the concentration n_S of free electrons in the plane of the adsorbent surface. Here $n_S \propto \exp(V_S/kT)$, so that

$$\frac{dN_A^-}{dt} = \lambda \exp\left(-\frac{V_s}{kT}\right). \qquad (12)$$

The author points out that if V_S is linearly related to N_A^- Eqn. (12) reverts to the Roginskii–Zel'dovich kinetic equation (1a), but if

$$V_s = V_s^0 - kT \ln[1 - (N_A^-)/(N_A^-)_{max}] \qquad (13)$$

the kinetic isotherm of Langmuir is obtained:

$$N_A^- = (N_A^-)_{max}[1 - \exp(-\alpha t)].$$

A similar expression for the rate of chemisorption is given by Weisz[47]: the rate of adsorption (of an acceptor gas) is proportional to the flux density of free electrons directed from the bulk towards the surface of the semiconductor, i.e. to the product of their surface concentration, their mobility, and the potential gradient at the surface.

Lastly, we shall discuss the work of Jantsch[48]. According to his model, a species landing on the surface from the gas phase is physically adsorbed and wanders on the surface until it is enabled to undergo charge transfer with the adsorbent at some surface defect. It is then converted into an ion, and this brings about the transition from the physically adsorbed to the chemisorbed state.

Furthermore, direct desorption of a chemisorbed species is considered to be very unlikely, such species disappearing from the surface only through transition to the physically adsorbed state. The kinetics of chemisorption are given by the equation

$$dN/dt = g - f. \qquad (14)$$

Here N is the surface concentration of chemisorbed species, g the increment of N per unit time resulting from transitions from the physically to the chemically adsorbed state, and f the decrement of N caused by the reverse process.

The expression for f is written in the form

$$f = N/\tau, \qquad (15a)$$

where τ is the average lifetime of a species in the chemisorbed state, and the expression for g is of the form

$$g = (\sigma z + N/\tau)w, \qquad (15b)$$

where z is the number of collisions of gas molecules with 1 cm² of the surface per second and w the probability of finding an adsorbed species in the chemisorbed state. The quantities τ, z, σ, and w are constant. We should note that the factor $(\sigma z + N/\tau)$ in Eqn. (15b) obviously expresses the increase in the concentration of physically adsorbed species per unit time. Expressing g in the form of Eqn. (15b) is equivalent to assuming that the rates of physical and chemical adsorption are in the ratio of $1 : w$. This hypothesis (whose justification is not clear) excludes the concentration of physically adsorbed species from (15b).

By inserting into Eqn. (14) the expressions (15a) and (15b) and integrating we can arrive at the Langmuir kinetic isotherm:

$$N(t) = \alpha[1 - \exp(-\beta t)],$$

where

$$\alpha = \sigma z \tau w/(1 - w); \qquad \beta = (1 - w)/\tau.$$

Thus, all the (theoretical) papers on the kinetics of chemisorption at semiconductor surfaces considered here have the following characteristic feature in common: they treat chemical adsorption as a charged form of adsorption. The possibility of a chemical bond between an electrically neutral gas molecule and the adsorbent lattice is completely ignored. This neglect of the neutral form of chemisorption is characteristic of the boundary layer theory, and can be taken to be its most serious defect.

It can be shown[42] that desorption of species directly from the charged state is much less probable than desorption of neutral species, and therefore exchange between the chemisorbate and the gas phase occurs almost entirely via the neutral form of chemisorption. On the other hand, the transition of a chemisorbed species from the neutral to the charged state can be the rate-limiting step in a number of reactions occurring at a semiconductor surface. Garrett[50] used this approach in his theoretical study of the rate of a reaction involving the mechanism

$$\mathrm{AeL} + \mathrm{DpL} \rightarrow \mathrm{ADL},$$

where A is an acceptor species and D is a donor species.

We should note, however, that in many of the papers discussed above physical adsorption is identified with the neutral form of chemisorption to a greater or lesser extent. This is specially true of the work of Germain[18], in which the function of the neutral form of chemisorption is wholly ascribed to a state which Germain terms physical adsorption.

III. THE ELECTRONIC THEORY OF CHEMISORPTION

1. Role of the Electronic Factor in the Kinetics of Chemisorption on a Homogeneous Surface

In the last three subsections of this article we shall discuss the role of the electronic factor in the kinetics of chemisorption on semiconductors from the standpoint of the electronic theory. We shall assume that chemisorbed species can exist at the surface either in an electrically neutral or in a charged state (corresponding to the "weak" and the "strong" surface bond respectively), and that transitions between the two states are possible. To make the discussion more concrete, we shall confine ourselves to the adsorption of acceptor species.

Let us examine the kinetics of chemisorption on a uniform surface[51], at constant temperature T and pressure P. Let N^0 and N^- be the surface concentrations of chemisorbed species in the neutral and in the charged states respectively. Assuming that only the species present on the surface in the neutral state can be desorbed, whereas the charged species do not undergo exchange in any way with the gas phase, we can write

$$\left.\begin{aligned} dN^0/dt &= (a_1 - a_2) - [(b_1 + b_4) - (b_2 + b_3)] \\ dN^-/dt &= (b_1 + b_4) - (b_2 + b_3) \end{aligned}\right\} \qquad (16)$$

where

$$\left.\begin{aligned} a_1 &= \alpha_1 P(N^* - N) & a_2 &= \alpha_2 N^0 \exp(-q^0/kT), \\ b_1 &= \beta_1 n_s N^0, & b_2 &= \beta_2 N^- \exp(-v/kT), \\ b_3 &= \beta_3 p_s N^-, & b_4 &= \beta_4 N^0 \exp[-(u - v)kT], \end{aligned}\right\} \qquad (17)$$

and

$$\alpha_1 = \varkappa/N^* \sqrt{2\pi MkT}, \quad \varkappa = \varkappa_0 \exp(-E_0/kT). \qquad (18)$$

Here a_1 and a_2 are the numbers of species adsorbed and desorbed per second from 1 cm² of the surface, b_1, b_2, b_3, and b_4 are the numbers of corresponding electronic transitions per cm² of the surface per second (see Fig. 5); N^* is the surface concentration of adsorption centres, i.e. the maximum number of species which can be adsorbed on 1 cm², q^0 is the energy required to detach a neutral species from the surface (the energy of the "weak" bond), M the mass of the adsorbed species, $\varkappa$ the capture probability of a species by the surface, E_0 the activation energy attending the formation of a "weak" bond, and n_S and p_S are the concentrations of free electrons and holes in the plane of the adsorbing surface (at $x = 0$); the significance of the quantities v and u is clear from Fig. 5.

We shall also use the symbols

$$\left.\begin{aligned} 1/\tau &= \alpha_2 \exp(-q^0/kT), \\ 1/\tau^0 &= \beta_1 n_s + \beta_4 \exp[-(u - v)/kT], \\ 1/\tau^- &= \beta_3 p_s + \beta_2 \exp(-v/kT), \end{aligned}\right\} \qquad (19)$$

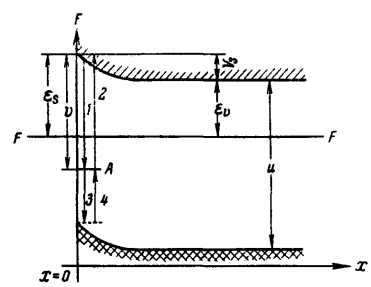

Fig. 5.

Note that $1/\tau$ defines the probability (per unit time) of desorption of a species; $1/\tau^0$ and $1/\tau^-$ are the probabilities of charging and discharging a chemisorbed species respectively. In other words, τ is the mean lifetime of a species in the adsorbed state, τ^0 and τ^- are the mean lifetimes of a chemisorbed species in the neutral and charged states respectively.

At low coverages, when

$$N \ll N^*, \tag{20}$$

the system of equations (16) can be written, using Eqns. (17)–(20), in the form

$$\left.\begin{aligned} \frac{dN^0}{dt} &= \frac{N^0_\infty - N^0}{\tau} - \left(\frac{N^0}{\tau^0} - \frac{N^-}{\tau^-}\right), \\ \frac{dN^-}{dt} &= \frac{N^0}{\tau^0} - \frac{N^-}{\tau^-}, \end{aligned}\right\} \tag{21}$$

where $N^0_\infty = N^0(\infty)$. We have made use of the fact that at $t = \infty$ we have $a_1 = a_2$, whence $\alpha_1 PN^* = N^0_\infty/\tau$.

Assuming that electronic quasi-equilibrium exists in the bulk of the semiconductor (i.e. that the distribution of free electrons and holes is approximately the equilibrium distribution corresponding to the instantaneous value of the surface charge), and that the electron and hole gases are non-degenerate, we can use equilibrium Boltzmann expressions for n_s and p_s. Under these conditions τ^0 and τ^- turn out to be functions of N^-.

If we solve the simultaneous equations (21) for constant τ^0 and τ^-, i.e. ignoring changes in the bending of the bands during chemisorption, we can analyse the kinetics of adsorption and desorption, and then proceed to show that the main features of the kinetics thus obtained do not alter appreciably when allowance is made for changes in the bending of the bands.

If electronic equilibrium exists at the surface at any given instant, t, the relative extents of the neutral and of the charged forms of chemisorption at that instant can be calculated by the well-known formulae of Fermi statistics:

$$\left.\begin{aligned} \eta^-(t) &= \frac{N^-(t)}{N(t)} = \left[1 + \exp\frac{\varepsilon_s(t) - v}{kT}\right]^{-1}, \\ \eta^0(t) &= \frac{N^0(t)}{N(t)} = \left[1 + \exp\frac{v - \varepsilon_s(t)}{kT}\right]^{-1}, \end{aligned}\right\} \tag{22}$$

where ϵ_S is the depth below the bottom of the conduction band of the Fermi level at the surface (see Fig. 5).

According to the relative values of the characteristic times τ, τ^0, and τ^-, electronic equilibrium can be preserved or destroyed during adsorption and desorption. The former regime (adsorption or desorption in which electronic equilibrium is maintained) is observed when

$$\tau^0, \tau^- \ll \tau. \tag{23a}$$

In this case (case *a*) the establishment of electronic equilibrium is fast in comparison with the establishment of adsorption equilibrium. Electronic equilibrium at the surface is set up long before adsorption equilibrium, and is maintained at all times. The second regime (case *b*) exists when adsorption or desorption causes a perturbation of the electronic equilibrium, i.e. when

$$\tau \ll \tau^0, \tau^-. \tag{23b}$$

In this case adsorption occurs in two distinguishable stages: first, equilibrium between the neutral form and the gas phase is rapidly set up, and then, in a second stage, the charged form appears whilst the concentration of neutral species remains stationary.

Either of these two limiting cases can occur in practice, depending on the nature of the adsorbent and of the adsorbate.

On the assumption that τ^0, τ^- = const, the kinetics of chemisorption after a short initial period take the form of the Langmuir equation. If allowance is made for the change in the bending of the bands during chemisorption, the kinetic isotherms usually depart from the Langmuir form. As long as electronic equilibrium is maintained, the departures from Langmuir kinetics appear only in the region close to adsorption equilibrium, whereas in the absence of electronic equilibrium these departures manifest themselves long before adsorption equilibrium is reached. Combining the two equations (21), we obtain

$$\frac{dN}{dt} = \frac{N^0_\infty - N^0}{\tau}, \tag{24}$$

whence it is evident that, as long as $N^0 \ll N^0_\infty$, the function $N(t)$ increases approximately as $N^0_\infty t/\tau$, as required by Langmuir kinetics, in the region far from adsorption equilibrium. In the case of electronic equilibrium the conditions $N^0 \simeq N^0_\infty$ necessarily implies that we are approaching adsorption equilibrium. When electronic equilibrium is disturbed, however, N^0 becomes comparable with N^0_∞ long before adsorption equilibrium is established.

The dependence of the activation energy for adsorption upon electronic parameters such as ϵ_v, V_S, and ϵ_S is quite different for the two cases *a* and *b*. If condition (23a) applies, then in the region far from adsorption equilibrium the activation energy is in general independent of the electronic parameters. This is evident from Eqn. (24), since when $N^0 \ll N^0_\infty$ we have

$$\frac{dN}{dt} = \frac{N^0_\infty}{\tau} = \alpha_1 PN^* = k\exp\left(-\frac{E_0}{kT}\right).$$

This situation obtains even if the charged form of chemisorption predominates in the adsorbate, so that the rate of adsorption is practically the same as the rate of generation of the charged form. This is not surprising if we remember that the rate of appearance of charged species (acceptors) is proportional not only to n_S but also to the concentration of unoccupied levels, i.e. the extent of the neutral form of chemisorption. It turns out that, if electronic equilibrium is maintained during adsorption and the chemisorbate is predominantly in the charged form, then the larger n_S the lower is the concentration of unoccupied levels at any instant: the net result is that the rate of appearance of charged species (and hence the rate of adsorption) becomes independent of n_S, i.e. of the position of the Fermi level.

The situation is quite different when electronic equilibrium is disturbed [case (23b)]. In the second stage, when the neutral species have reached equilibrium with the gas phase and the charged form of chemisorbate is being produced, the activation energy for adsorption includes the term ϵ_S. Under these conditions we are far from adsorption equilibrium. The rate of adsorption is given by the expression

$$dN/dt = k_0 \exp(-\varepsilon_s/kT).$$

It can be shown that this formula remains valid even when changes in band bending during adsorption are allowed for. By inserting various alternative forms of the function $\epsilon_S = \epsilon_S(N)$, we obtain various kinetic isotherms not of a non-Langmuir form. The following relationships have been observed experimentally[13]:

$$\varepsilon_s = AN + B \text{ and } \varepsilon_s = A' \ln N + B'.$$

The form of the function $\epsilon_S = \epsilon_S(N)$ has been studied theoretically by Kuznetsov[52].

2. Partial Irreversibility of Chemisorption on Semiconductors

It is well known that desorption at the temperature of the adsorption experiment does not always remove the whole of the chemisorbate from the surface. This phenomenon is termed partial irreversibility of chemisorption. We shall consider here two possible mechanisms[53,54].

The first mechanism stems directly from the model of desorption proposed for the case where electronic equilibrium is disturbed. Thus, in case *b* [see condition (23b)] the desorption of charged species lags very considerably behind the desorption of neutral species: after a time of the order of τ practically all the neutral species have left the surface, whereas the desorption of charged species is protracted over a much longer time interval, of the order of τ^-. An important consideration here is that τ^- can be very large: values of the order of 10^4–10^5 s have been computed. In this case the duration of a practical desorption experiment can be small compared with τ^-, i.e. with the time needed to remove the charged species, and hence also with the time needed for complete desorption of the chemisorbate. In these circumstances we shall be able to observe, in practice, only the desorption of the neutral form, and the charged form will appear to be almost irreversibly bound to the surface. We should note that if we abandon the assumption that only a small fraction of the adsorption centres is occupied [see Eqn. (20)], then the time for complete adsorption is found to be much less than the time for complete desorption.

The second mechanism consists in the reaction between the chemisorbate and an impurity present in the bulk of the semiconductor. For example, in the chemisorption of oxygen on ZnO the ionised interstitial zinc Zn_i^+ arriving at the surface from the bulk can react as follows with a charged, chemisorbed oxygen atom O_a^-:

$$Zn_i^+ + O_a^- \rightarrow Zn^{2+}O^{2-}.$$

This process is equivalent to an irreversible addition to the crystal lattice resulting from oxidation of the zinc in excess of stoichiometry. Many authors[30,35,45,55] have discussed the role of processes of bulk impurity extraction in chemisorption.

The most characteristic difference between the two mechanisms is that the irreversibility associated with the first is only "apparent": if desorption is allowed to proceed for a long enough time the charged form of chemisorbate ion will also be removed from the surface. On the other hand, the irreversibility associated with lattice addition can be regarded as "true" irreversibility. Furthermore, "apparent" irreversibility effects can be expected only at not too high temperatures, since τ^- falls off rapidly with increase of temperature. On the other hand, the "true" irreversibility mechanism requires a high enough mobility of the reacting impurity, and should therefore be undetectable at low temperatures, its contribution increasing sharply with increase of temperature.

Many experimental observations can be accounted for by either of these two mechanisms (for example, the large extent and large irreversibility of the adsorption of oxygen on ZnO specimens with a high content of interstitial zinc, which does not affect, however, the initial rate of desorption[30]). Therefore, it is interesting to distinguish experimentally between these two mechanisms of irreversible adsorption and to identify the mechanism which is operative under some particular experimental conditions. We shall now consider the appropriate criteria, making the following assumptions: the reaction is so slow that the equilibrium (Boltzmann) distribution of the reacting impurity in the bulk of the solid is not disturbed; chemisorption (or, more precisely, the appearance of charged species on the surface) is fast in comparison with the diffusion of the reacting impurity towards the surface; the amount of impurity removed is small in comparison with the total amount of reacting impurity in the crystal.

Based on these assumptions, the following criteria for distinguishing experimentally between "true" and "apparent" irreversibility have been obtained.

1. Let N_r and N_i stand for the reversible and the irreversible contributions to the chemisorption respectively. "Apparent" and "true" irreversibility lead to different relationships, other conditions being equal, between the ratio N_i/N_r and the bending of the bands at the surface (V_S).

In the case of "apparent" irreversibility

$$N_i/N_r \propto \exp(-V_s/kT),$$

whereas if the irreversibility is "true" and the charged form of chemisorption predominates, the expression becomes

$$N_i/N_r \propto \exp(+V_s/kT),$$

or, if the neutral form predominates in the case of "true" irreversibility,

$$N_i/N_r = \text{const}.$$

2. The kinetics of the change in the electron work function (φ) and in electrical conductivity (σ) of the adsorbent are different in the two cases. In the case of "apparent" irreversibility we should find partial irreversibility of φ (since the neutral species are desorbed, the charged species remain on the surface, and both contribute to the change in φ) and complete irreversibility of σ (since σ is determined only by the concentration of charged species, which remain on the surface, see curves *2* of Fig. 6). However, if the chemisorption is "truly" irreversible, we should observe complete reversibility of both these quantities (curve *1* of Fig. 6). In this case, both neutral and charged species are removed from the surface, since the absorption of charged species by an impurity is equivalent to their removal from the surface as regards their effect on φ and σ. Thus, direct adsorption measurements are necessary in order to identify true irreversibility.

Of course, the above statements are correct only if the surface reaction does not influence too strongly the spectrum of surface states due to causes other than adsorption.

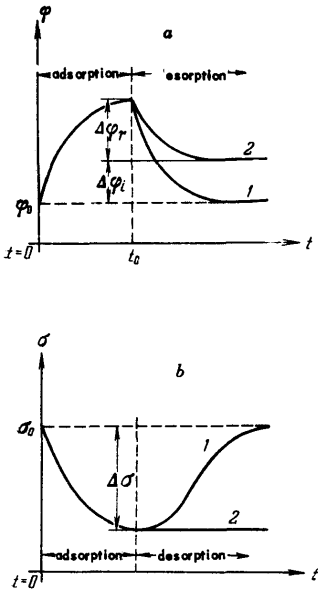

Fig. 6.

We should also remember the assumption that the impurity is effectively inexhaustible, so that ϵ_v remains constant.

An "apparent" irreversibility mechanism is evidently involved in the adsorption of oxygen on TiO_2 at room temperature: this is shown by the changes in φ and σ during desorption recently reported by Figurovskaya[56]. A "true" irreversibility mechanism can be observed at temperatures as low as 350° on zinc oxide, as reported by Glemza and Kokes[57], who made a combined study at this temperature of the adsorption of oxygen on ZnO and of the kinetics of changes in σ.

3. Electronic Aspects of the Inhomogeneity of the Adsorbent Surface

The idea of inhomogeneity in the adsorbent surface arose from attempts to explain the large fund of experimental data which do not fit into the simple model of adsorption phenomena developed by Langmuir. The theory of adsorption and catalysis at inhomogeneous surfaces, due mainly to Roginskii's school[58,59], assumes that different portions of the surface differ in their adsorption properties: their adsorption parameters (such as the heat of adsorption and the activation energy) are not the same everywhere, but each element of area shows simple (Langmuir) behaviour. Surface inhomogeneity is characterised by a definite distribution function of the elements of area with respect to activation energy and heat of adsorption.

It should be noted that the universality of the initial Langmuir model is lost[60] when allowance is made for the electronic processes taking place at the surface during chemisorption. In the electronic theory of chemisorption the adsorption and kinetic laws are not, generally speaking, of the Langmuir type, even for a uniform surface and in the total absence of direct interaction between chemisorbed species. This is because in the treatment of the adsorbent–adsorbate system as a unified quantum-mechanical system the species are "made aware" of each other through the electron gas of the adsorbent. Thus, the concept of inhomogeneity is only an additional cause for departure from the Langmuir laws.

We shall attempt here to deal with the case where the initial adsorption behaviour of the homogeneous elements of surface is non-Langmuir. In other words, the contribution of chemisorption to the surface charge is assumed small, and therefore the variation of ϵ_S with N is ignored. Only in this case can the inhomogeneity of the adsorbent surface be characterised by a distribution function specific to the surface itself: in the more general case the "distribution function" is a characteristic of the combined adsorbent–adsorbate system[60]. This approximation is equivalent to separating the effects of surface inhomogeneity and surface charging during chemisorption[61,62].

The basic problem facing the theory of adsorption and catalysis at inhomogeneous surfaces is to clarify the physical significance of the distribution function by which the theory operates. The question is: why do the different elements of surface show different activation energies or heats of adsorption? According to the ideas of the electronic theory, the adsorption properties of any part of the surface are determined by the electronic state of the system, i.e. by the position of the Fermi level in that particular element of area. Therefore, any mechanism causing the position of the Fermi level (relative to the energy bands) to vary from point to point on the surface can serve as a physical basis for surface inhomogeneity. In particular, inhomogeneity can result from uneven distribution of impurities in the bulk and at the surface of a semiconductor (even when we are dealing with impurities of a single kind). In practice, the topography of the Fermi level at the surface, i.e. its position with respect to the energy bands, is uniquely determined (as a function of position along the surface) by the distribution of impurities in the semiconductor. We must stress that the impurity in question can be one not directly involved in chemisorption (i.e. not playing a direct part in the act of chemisorption). For example, it may be an impurity located in the bulk phase. The concept of an impurity uniformly distributed in a semiconductor, widely adopted in theoretical papers, is of course greatly idealised. The inhomogeneity of the electronic properties f a semiconductor surface is a well-known fact[63–65].

As an illustration of what has been said, we shall consider the adsorption isotherm, which for a uniform surface is of the form

$$N/N^* = \theta = [1 + (b_0/P)\exp(-q/kT)]^{-1}, \qquad (25)$$

where, according to Vol'kenshtein[42],

$$q = q^0 - kT\ln\eta^0(\varepsilon_s).$$

Obviously, surface inhomogeneity implies that different areas will have different values of q. It is with respect to this quantity that averaging is carried out in the theory of adsorption at inhomogeneous surfaces. All the distribution functions which are compared with experimental adsorption isotherms in the theory are, in fact, distribution functions with respect to q. As long as we remain within the boundaries of Langmuir's molecular-kinetic model, i.e. as long as we ignore the electronic processes attending chemisorption, we have $\eta^0 = 1$, and therefore the quantity $q = q^0$ has the significance of a bond energy between the

chemisorbed species and the surface. Under these conditions the isotherm (25) is indistinguishable from the familiar Langmuir isotherm

$$N/N^* = \theta = (1 + b/P)^{-1},$$

where

$$b = b_0 \exp(-q^0/kT),$$

and any inhomogeneity results from local differences in the energy q^0 between the chemisorbed species and the surface, and can therefore be characterised by a distribution function with respect to q^0.

In the electronic theory of chemisorption differences in bond energy q^0 are not excluded, but they do not play the major role. Local differences in the position of the Fermi level ϵ_S are also possible. This will give rise to differences in the value of q for different elements of the surface, even if the bond energy q^0 is the same everywhere. In this case the surface inhomogeneity will be characterised by a distribution function with respect to ϵ_S.

In order to apply to an inhomogeneous surface a kinetic isotherm obtained for a uniform surface, some sort of averaging over a parameter of the equation is necessary. It can be shown that local differences in the part of the activation energy E_0 which does not depend on electronic parameters (i.e. differences in the capture probability of a species by the surface) do not cause departures from the Langmuir form of the kinetic isotherm (at low coverages). Non-Langmuir isotherms can be obtained in two ways, either by assuming local differences in the position of the Fermi level or by assuming local differences in the energy needed to remove a neutral species from the surface. Differences in ϵ_S may or may not lead to non-Langmuir kinetic isotherms, depending on the relative values of the time--constants τ, τ^0, and τ^-, and also on the position of the local chemisorption level with respect to the surface Fermi level. An important consideration is that if adsorption (of acceptor species) occurs under conditions such that electronic equilibrium is not maintained, and only the conduction band takes part in electron transfer processes at the surface, non-Langmuir kinetics can arise after some initial time interval only from differences in surface charge, i.e. from the fact that the kinetic isotherm was not of the Langmuir form even for a homogeneous surface. If the kinetic isotherm in this case is of the Langmuir type, i.e. of the form

$$N = A[1 - \exp(-kt)],$$

the coefficient k depends only on the position of the level associated with the chemisorbed species relative to the energy bands, and hence no averaging process can alter N.

It is clear that the role of the electronic factor in the kinetics of chemisorption on semiconductors is radically different according to whether electronic equilibrium is or is not maintained; the most characteristic kinetic features, established experimentally, are indeed those which refer to the case of disturbed electronic equilibrium. These include: (1) the non-Langmuir character of the kinetic isotherms, whose shape is determined, as shown by the work of Enikeev, Margolis, Roginskii, Rufov, and others, by the form of the function $\epsilon_S = \epsilon_S(N)$, i.e. by the way in which the work function varies with coverage; (2) the dependence upon electronic parameters of the activation energy for adsorption. Thus, the assumption that electronic equilibrium is maintained during chemisorption is far from always being justified, and is not a theoretical necessity.

Further progress in the study of kinetics, and therefore also of chemisorption on semiconductors, must await new investigations, particularly experimental ones, of the kinetics of chemisorption (in the usual meaning of the word) coupled with a study of the accompanying changes in the electronic state of the adsorbent and of the species held on its surface.

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ELECTRONIC PROPERTIES AND STRUCTURE OF POLYMERIC ORGANIC SEMICONDUCTORS

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I. INTRODUCTION

Polymers with conjugated bonds occupy a central place in an interesting new class of compounds, that of organic semiconductors, which includes also low-molecular-weight one-component compounds with conjugated bonds (for example, condensed aromatic systems, dyes, etc.), individual charge-transfer complexes, some biological materials such as proteins, and charcoals. The intensive research devoted to these polymers, which were first synthesised as recently as the late 1950's,[1-4] has aroused wide interest in the problem and has created a borderline science: the physics and chemistry of organic semiconductors†. The main attraction of polymers in this context is the fact that their chemical configuration and their structure can be modified as required, thus providing an unlimited number of materials on which to study the nature of the specific properties of organic semiconductors and the modification of these properties in a desired direction.

In recent years, many reviews and monographs have been written on the methods of preparation[24-27] and on the properties[13-17,21,28-37] of semiconducting polymers. It is now recognised that polymers with conjugated bonds, like organic semiconductors of other classes, have a specific type of electronic and atomic structure which gives rise to a combination of properties uncommon in organic compounds: a special electrical and magnetic behaviour, high thermal stability, low solubility, reactivity of a specific kind (in particular, catalytic activity‡), etc. In the present review, which includes all work published up to January

† Progress in the study of organic semiconductors of various classes has been discussed in a number of books and reviews[5-23].

‡ Papers on the catalytic properties of semiconducting polymers, already fairly numerous, will not be considered here because of lack of space. See, for example, Refs. 38–43 and also p.778.

1966 (and a few more recent papers), we shall be primarily concerned with the electrical, magnetic, and structural studies of polymers with conjugated bonds of the classes listed below.

CARBO-CHAIN POLYMERS

A. With Acyclic or Alicyclic Conjugation Chain

1. Polyvinylene ("polyacetylene"), prepared by dehydrochlorination of poly(vinyl chlorides) (PVC),[1,44-55] dehydration of poly(vinyl alcohols) (PVA),[56-62] polymerisation of acetylene[63,64] and polycondensation of acetaldehyde[65,66].

2. Substituted polyvinylenes: poly(phenylacetylene)[2,3,65,67-75] and others[38,39,64-66,76-90].

3. Polyacetylene (poly-yne): $-[C\equiv C]_n-$ or $=[C=C]_n=$.[61,91-93]

4. Poly(cyclopentadiene)[95-97].

B. With Aromatic Rings in the Conjugation Chain

1. Polyphenylene[64,67,71,98-101], polyphenylene–polyvinylenes[102,103], and block copolymers of polyphenylene[98,104,105].

2. "Polybenzenes", polynaphthalenes, and other polyacenes[64,87,97,106,107].

3. Poly(arylenequinones)[67,108-111].

4. Polyarylene-polyacetylenes with triple bonds in the conjugation chain[39,61,91,112-124].

HETERO-CHAIN POLYMERS

1. Containing nitrogen in the conjugated chain: poly(acrylonitrile)§ (PAN)[41,48,78,125-147] and other polynitriles[66,132,148-159], paracyanogen[132], poly(azophenylenes)[67,99,105,160-167,217,392,393], poly(Schiff bases)[132,168-177], polyazines[175,178-180], poly(aryleneamines)[181-185], poly(aminoquinones)[186-188], poly(azoarylenequinones)[189], polytriazines[67,190], polypyridines[191-196], polypyrrole¶[197,198], poly(tetracyanoethylene)[155,199-201], aniline black[172,202,203] and others[49,196,204-210].

2. Containing oxygen in the conjugated chain: polyxanthenes or poly(acenequinone) radicals[48,100,172,208,211-216] and others[16,48,50,124,178,180,217,218].

3. Containing sulphur in the conjugated chain[107,178,180,208,217,219,220].

Various chelate polymers¶ with N, O, and S atoms in the conjugation chain have also been investigated (see, for example, Refs. 221–224).

§ The system of conjugated bonds and the semiconducting properties appear only after heat treatment.

¶ It must be emphasised that these polymers retain their specific electrical and magnetic properties even when the continuous conjugated chain in the molecule is interrupted by bridges of the hetero-atoms or by other groups ($-CH_2-$, $-SO_2-$, biphenylene, etc.): see next column and p. 776.

CHELATE POLYMERS (POLYCOORDINATION COMPOUNDS)

This group includes the poly(phthalocyanines)[225-232], poly(tetracyanoethylenes)[97,200,233-243], polyferrocenes[17,67,208,156,216,244-249], and others[58,67,112,186,221-224,250-268]. These polymers are based on chelate complexes of both transition metals (Cu, Fe, Co, Ni, Mn, etc.) and non-transition metals (Mg, Zn, Cd, Hg).

OTHER TYPES OF SEMICONDUCTING ORGANIC POLYMERS

1. Products of the radiation–thermal treatment of polyethylene[269-279] and poly(acrylonitrile)[131,280].

2. Compositions including polymers and metallic powders[231,281-288].

3. Complexes formed by various polymers with halogens[74,174,185,197,198,205,211,289-294] and with other organic substances[51,295,296], with organic molecules[185,290,295,297,298], and also with O_2.[74,195,198,275]

II. SPECIFIC PROPERTIES OF SEMICONDUCTING POLYMERS

1. Chemical Structure of the Molecule and Structure of the Material

The electronic properties of solid organic compounds able to crystallise only in the form of molecular lattices are determined, on the one hand, by the properties of the separate molecules and, on the other hand, by the way in which these molecules are packed and by their mutual interactions, i.e. by the parameters of the solid as a whole. It is best to consider these two factors separately.

From the point of view of the chemical structure of the molecule, the principal feature common to all semiconducting polymers is a system of conjugated π-bonds. The properties of such a system reveal themselves: (1) in the colour of the material, which becomes deeper as the degree of conjugation in the molecule increases (and can become black, for example after heating to 400°)[3,45,59,64,72,121,122,177,299] and less intense when the conjugation is perturbed[45,122,123,125,180]; (2) in the infrared spectra (appearance of new characteristic bands[49,59,60,83,91,93,129,239,299,301] and sharp increase in background absorption[98,239,248,302,303]); (3) in the u.v. spectra (development of strong characteristic absorption[133,134,167,242]) and in the fluorescence spectra[69,304-306]; (5) in the electrical properties (see Section II, 2).

However, recent work has shown that the earlier views, according to which the molecule of a semiconducting polymer can be visualised as a one-dimensional crystal with an uninterrupted system of conjugated π-bonds[30,307], are incorrect. There is abundant evidence for this statement. The usual sequence of colour changes of polymers subjected to heating and irradiation (yellow to brown) is not what we would expect from a gradual increase in length of the conjugated system (yellow, red, purple, blue)[52]. Heating of the polymers does not give rise to a clear long-wave shift of the absorption maximum in the u.v. spectra, but only increases the intensity near the long-wave edge of the band[133,134,242]. Heat-treated poly(methyl vinyl ketone)[300], unlike PAN[299], does not show a long-wave shift in the infrared spectrum. The electrical properties are not seriously

impaired[81,122,124,164,165,175,176,178,180,184] when the conjugation in a polymeric chain is destroyed by introducing bridging groups such as CH_2, O, N, and the biphenylene grouping, whose rings have been shown by NMR not to be coplanar[99]. Finally, it is clear from the fluorescence spectra that an increase in molecular weight is not accompanied by an increase in the length of the conjugated system[69], and the ESR spectra, which sometimes show a hyperfine structure for solutions[49,185], indicate that the unpaired electron is delocalised only over 2–7 monomer units[56,68,74,128].

It follows that the continuous conjugated chain in semiconducting synthetic polymers is usually of limited length (probably only a few monomer units). Whatever the cause of this phenomenon† we must conclude that the minimum length of uninterrupted conjugated system of π-bonds needed to give rise to the specific electronic properties of the polymers is no greater than the size of the conjugated systems in low-molecular-weight one-component compounds and in individual charge-transfer complexes. This conclusion is an argument for the general similarity of the electronic nature of all organic semiconductors.

Before proceeding to a discussion of the solid-state structure of semiconducting polymers, we must stress the fact that this structure is composed of oligomeric molecules. Thus, most workers have been unable to obtain a molecular weight higher than 3000, or a degree of polymerisation in excess of 10.[2,83,120,122,160,185,194,195,308,309] According to Berlin[15,160,309], this "oligomericity" is due to a gradual deactivation of the radicals with increasing length of conjugated chain, arising from the increasing delocalisasation of the unpaired electron. However, not all polymerisation processes involve radicals [for example, the dehydration of poly(vinyl alcohol), the dehydrochlorination of poly(vinyl chloride), "onium" polymerisation], and we can therefore envisage gradual deactivation of any reaction centre — not just free radicals — or focus attention on the decrease of the solubility of the product with increasing degree of polymerisation[308], particularly since polymers with conjugated bonds are prone to association in solution (anomalous viscosity).

Because of their low molecular weight, semiconducting polymers can exist not only in the amorphous state but also as crystals with a molecular lattice‡[61,122,135]. Intermolecular interactions in this type of lattice are fairly weak on the whole, as shown by the poor electrical conductivity of the crystalline polymers and also by the instability of the lattice towards heating: the oligomer usually becomes amorphous even at 200–300°,[57,59,60,122,161,310] although some increase in crystallinity can be observed in the initial stages (below 200°)[57,59,310,311].

However, stable local formations exist within the weak lattice, as evidenced by the ESR signal in solution[3,49,68,83,105,195,306,312], from which we can deduce that the concentration of unpaired spins has not changed[3,68,195], by the anomalous viscosity at high dilutions[135,160–162,184,190,195,313], and by the identity of the electronic spectra in the solid state and in solution, all of which have been observed for charge-transfer complexes based on polymers[293]. The nature of these stable formations is discussed tentatively in Section III.

The ease with which the molecular lattice of polymers collapses on heating is due not only to the instability of lattices of this type but also to the fact that a specific amorphous structure is produced[47,59,61,98,122,175,181] in which interaction between π-electron systems and the polar groups of oligomeric molecules can readily occur. This is apparent both from the observed chemical processes[59,60,129,133,134,146,170,299,300] and from the electrical and magnetic properties discussed in Section II, 2 and II, 3. The overall conclusion from the available data is that the specific structure of semiconducting polymers is due to regions with a relatively large number of conjugated bonds (usually, systems of condensed aromatic rings) separated by disordered regions in which the conjugation is weak[47,85,122,128,135,145,191,200,227,237,242,269,270,275] (see p. 780).

Heating to high temperatures (upwards of 500–600°) produces a gradual increase in the size of the conjugated regions and slowly raises the degree of order of the structure[47,59,123,144,146,147,275,314,315], i.e. it makes the properties of the polymers closer to those of charcoals. Of course, crosslinking processes and the formation of a three-dimensional structure can be rather slow[78,120,316]. In particular, a correlation has been found[61,91–93,314,317] between the structure of the pyrolysis products and the structure of the monomer unit in the starting molecules, and it has been shown that carbons can be obtained with a chain (poly-yne or cumulene) rather than a floor-block structure.

It will be clear from the subsequent discussion that, in order to understand the general features of the behaviour of semiconducting polymers, we need to make allowance for the interplay of the two factors considered here: the chemistructure of the molecule and the structural ordering of the material[124,165,175].

2. Electrical Properties

The electrical characteristics of polymers with conjugated bonds can vary widely: from those of dielectrics (as in the case of low-molecular-weight organic semiconductors and weak charge-transfer complexes) to those of semimetals (as in the case of strong charge-transfer complexes and carbons). Values of the electrical conductivity σ vary from 10^{-15} to $10^{2}\ \Omega^{-1}\ cm^{-1}$; the activation energy for conduction E_σ varies from 2 to 0.01 eV§. The variation of σ with reciprocal temperature is typically that expected for a semiconductor: the electrical conductivity increases exponentially with temperature T according to the law

$$\sigma = \sigma_0 e^{-E_\sigma/kT}.$$

The absence of polarisation effects during the passage of current is evidence that the conductivity is electronic rather than ionic[57,58,111,172,198,201,214,272,295]¶. The electrical properties are strongly influenced by the adsorption of oxygen[78,85,122,127,135,176,198,229,247,248,259,290]† and other substances[48,51,57,181,197,198,205,225,259,270], and also by

† In all probability, it is due partly to the low degree of polymerisation characteristic of polymers with conjugated bonds (see below) and partly to spontaneous disturbances occurring during the synthesis of the conjugated system.

‡ Some observations suggesting a correlation between the degree of crystallinity and the structure of the molecule have been reported[61,122,165,175]. It is interesting to note also that some degree of preferential orientation of the macromolecules can be induced in weakly crystalline polymers by pressure or by stretching[57,128,130].

§ For a number of polymers, semimetal characteristics have been reported[132,172] ($E_\sigma \leq 0$).

¶ Some workers discuss the possibility of ionic conduction[54,111,129,201,272,312], although polarisation effects do not necessarily imply an ionic mechanism[111].

† However, oxygen effects are often absent[57,68,154,178,179,181].

pressure [177,215,294,318], illumination (see p. 777), and irradiation [131,272,319]. When the resistance is not too high, surface conduction does not appear to distort the results [57,135,217]. But some workers point out that measurements with d.c. do not give a sufficiently complete picture of the electronic properties of polymers [200,237]. Nevertheless, the main conclusions derived from measurements with a.c. [144,200,201, 233,237,238,243,268,269,271,277] and with d.c. (see Section IV) are identical, and the results obtained by d.c. and a.c. measurements of the conductivity of poly(phthalocyanines) [230] are indistinguishable: we can therefore accept the d.c. method (which has been used in the vast majority of investigations of organic semiconductors) as entirely correct. Since the exact mechanisms of electrical conduction are not yet fully understood (see Sections IV and V), we cannot unequivocally ascribe the breaks often observed in the linear plots of $\log\sigma$ against $1/T$ to transition from impurity conduction to intrinsic conduction, particularly since Pohl's calculations for poly(acenequinone) radicals [172,214] would appear to exclude the possibility of impurity conduction by extraneous contamination. In general, with systems as inhomogeneous as polydisperse conjugated polymers it is hardly meaningful to talk of intrinsic conduction, and the term "impurity conduction" [145,277] can only refer to the presence in these polymers (excluding high-temperature polymers) of molecules or regions with a degree of conjugation sufficient to ensure appreciable ionisation at ordinary temperatures, the fraction of the total mass involved being small. Ohm's law has often been found to hold up to 10^3–10^4 V cm^{-1} in studies of semiconducting polymers [169,179,201], although departures are occasionally reported [64,214] at quite small fields of the order of 10–100 V cm^{-1}.

The sign of the current carriers (from measurements of thermo-e.m.f.) can be either positive or negative. However, oxygen always affects the thermo-e.m.f. in the positive direction [127,135,136,154,229,269], and it is at least possible that the current carriers, in contrast to the early views on organic semiconductors [5], consist largely of electrons (as indicated by most of the measurements in a vacuum), conduction by positive holes being the result of O_2 adsorption. It is interesting to note, however, that it has been possible to realise a true p–n junction in some polymers [271,320].

The electrical properties of polymers are determined by two factors: the structure of the molecule and the structure of the material. As regards molecular parameters, the necessary condition for semiconductivity in organic substances is the presence of a system of conjugated π-bonds in the molecule. As the number of π-electrons increases, we expect a decrease in ionisation potential, an increase in electron affinity [75], and an increase in polarisability, as has been established in a series of low-molecular-weight compounds with condensed rings [142]. In the case of polymers, this leads to improved electrical characteristics as the number of conjugated multiple or aromatic bonds in the polymer chain increases [45,59,61,129,133 134,167,177,214,221,253,257], and to the opposite effect when the conjugation is disturbed by lack of coplanarity of the aromatic rings [81,122,124,175,184,217,253] or by introducing into the conjugated chain aliphatic bridges, oxygen bridges, or sulphur bridges [122,124,164,165,175,176,178,180,217,319]. Pohl [172] observed an increase in conductivity with the number of aromatic π-bonds in poly(acenequinone) radicals, analogous to Eley and Parfitt's‡ rule for low-molecular-weight organic compounds [7,321,322]. Another analogy with low-molecular-weight conjugated systems — the increase in electrical conductivity§ following the introduction of nitrogen atoms into the conjugated chain [30,171,192,196,230] — is explained by the easier delocalisation of the π-electrons and also by the increased polarity of the molecules (see p. 780). The conjugated π-electron system ensures high values of the dielectric constant [29] and of the polarisability [323]. The structure of the molecule can influence the electrical properties also through changes in intermolecular interactions: introduction of side-substituents degrades the conductivity [108,110,217,228], and greater flexibility of the chain improves the electrical conductivity by facilitating intermolecular contacts [165,180,249,324].

The dependence of the electrical properties on the structure of the polymer as a whole is made evident, for example, by the improvement resulting from more ordered packing of the molecules [63,232,238] and by the effect of pressure cycling [128,130,144], both of which are attributed to changes in the properties of the intermolecular barriers [128,130,232]. On the other hand, instances have also been reported [59,61,122,175] of a decrease in resistance with decrease of the degree of crystallinity, associated with the lack of coplanarity of neighbouring condensed rings in the crystalline polymers [175] or with the break-down of the molecular crystal lattice [122]¶. On occasions, the degree of order has no particular influence on the electrical properties [57,59,178,295]. This masking of the role of the structure can be ascribed, on the one hand, to the well established competition between ordering in the material and conjugation within the molecule [165,180] and, on the other hand, to the effect of adsorbed gases.

On the question of the relative roles of order and conjugation, it is clear that greater flexibility of the molecular chains must result in closer packing and in conditions more favourable to intermolecular electron transitions, which determine the electrical properties of organic semiconductors (see Section IV). However, the introduction into the conjugated chain of groupings conducive to greater flexibility (in particular, methylene links) destroys the conjugation within the molecule and hampers the loosening of electrons. Thus, we find that single $-CH_2-$ groups introduced into the conjugated chain may increase the degree of crystallinity and improve the electrical properties by assisting intermolecular transfer, whereas longer links such as $-CH_2CH_2-$ degrade the electrical properties by lowering the degree of conjugation in spite of the fact that the degree of order is even higher [165,180]. The fact that the electrical properties are not improved indefinitely by increasing the number of double bonds in the polyene chain of a series of compounds [325,326] is further evidence that intermolecular electron transfer is the limiting stage in the conduction process.

Changes in electrical properties associated with adsorption can be identified by their reversibility.

‡ However, the electrical conductivity is reported to remain constant [64] in the series polybenzene–polynaphthalene–polyanthracene.

§ An increased conductance with partial removal of nitrogen from the polymer has been observed with poly(copper phthalocyanine) [230], but under these conditions the structure probably suffers considerable change. Weiss and coworkers [196] assume that an improvement in electrical conductivity due to nitrogen can be expected only when all the nitrogen groups exhibit either purely acceptor or purely donor properties.

¶ We should note that the more crystalline polymers are usually found to be poorer conductors than the amorphous polymers [61,122, 168,175].

Adsorption effects have been demonstrated, in particular, by measurements after heating *in vacuo* [78,127,130,135,136,247,248]. Some workers have been able to ascribe changes in conductivity to a specific adsorbate: O_2,[64,78,85,176,198,229,230,259,269] H_2O,[57,181,225,239] and ethylene [196,198]. The adsorption of O_2 was found, in most cases, to increase both the resistance and the activation energy for conduction in both *n*-type and *p*-type polymers† [64,78,85,176,198,229,259], as had been previously observed with dyes. The effect of O_2 decreases with increasing temperature of preliminary heat-treatment, and the electrical properties of polymers heated above 600–800° are no longer influenced by O_2 adsorption [85,269]. Since these effects are independent of the conductivity type of the material, we can assume, by analogy with the effect of iodine adsorption on the electrical properties of polymers [198,270,271], that O_2 acts by altering the conditions for electron transfer between highly conjugated regions rather than by affecting the concentration of current carriers [85,270,271] (see also p. 778 and 779)‡.

Occasionally, however, the reversibility of adsorption effects is highly hindered [248], and in many cases changes in electrical conductance arise from the evolution of volatile bulk impurities rather than from surface desorption: the process becomes irreversible even though no structural rearrangements are involved [129,184,227]. Some workers even hold the extreme view [78,129,136,248] that in pyrolytic materials any observed activation energy for conduction significantly different from zero must be associated with adsorption processes only, and not with the true electronic nature of the polymers. However, many workers have unambiguously related changes in electrical conductivity to reversible and irreversible structural changes rather than to adsorption [47,59,61,63,122,128,130,175,225,238,269].

Heat-treatment of the polymers breaks down the molecular crystals and leads to the formation of a specific structure with a low degree of order (see p. 775): this can cause an improvement in electrical properties even at relatively low temperatures (200–400°) by favouring growth of polyconjugated regions and by strengthening their mutual interactions [47,59,61,85,121,123,157,176]. However, in the early stages of heat-treatment (up to 200–300°) this disordering process often produces an irreversible increase§ in resistance [58,110,111,133,172,179,249], sometimes even despite a concurrent increase in the conjugation within the molecule [144].

It is interesting to note that the absolute values of the thermo-e.m.f. decrease irreversibly with increase of heat-treatment temperature [127,140,145,176,272], in keeping with the general tendency for the thermo-e.m.f. to fall as the electrical conductivity rises [129,184,227,328,329].

It follows from the above considerations that a very long conjugated chain in the molecule and long-range order (or crystallinity) in the structure of the polymer are far from being essential to the development of semiconducting properties. However, a recent theoretical investigation by Little [330] has shown that a new and astonishing physical phenomenon, superconductivity at ordinary temperatures, should appear if both these conditions are satisfied (namely, the creation of a stereoregular polymer in which specially chosen substituents maintain the excited state in an ideal polyene chain, coupled with the arrangement of the molecules in a specific type of long-range order.

Some groups of semiconducting polymers show still further peculiarities in their electrical properties. In particular, the behaviour of chelate polymers is determined by factors common to all organic semiconductors (electrical characteristics superior to those of the monomer [254], influence of the ligands [221,253], exchange interactions [224]), but it is also determined by the nature of the metal [221,224,253,254,264,265,267], although the role of this factor is sometimes a minor one [138].

Many polymers with conjugated bonds show photoelectric activity [83,87,114–117,121,133,167,169,179,214,224,259,276,331–333], generally similar to the well characterised phenomena in other classes of organic semiconductors [83,116,117,169]. In most cases the photoconductivity has been shown to be electronic in origin [83,114,117]. Some anomalies have also been observed, for example, the quenching of photoconductivity by oxygen in a *p*-type semiconductor [114,116] and polarisation phenomena [169]. Unfortunately, only a few polymers show appreciable photoeffects [116].

Other characteristic features of the electrical behaviour of semiconducting polymers will be discussed in the context of conduction mechanisms (Section IV). At this stage we shall only mention the compensation effect (linear relation between E_σ and $\log\sigma_0$) observed in a number of polymers [29,64,67,167,267,334,335], low-molecular conjugated systems [67,323,325], charge-transfer complexes [7,67], and dielectrics [336,337]. According to Tal'roze and Blyumenfel'd [334,335], this relationship is characteristic only of poor semiconductors, and should not be obeyed by low-resistance polymers [121,126].

3. Static Magnetic Susceptibility and Broad-Line ESR

Many polymers with conjugated bonds show large positive values of magnetic susceptibility [104,121,160–162,184,187,190,244,246,249,303,338–340], a dependence of the susceptibility on the field [121,161,162,181,244,246,249,312,340], and saturation at relatively low fields [249,312], i.e. the properties of an antiferromagnetic below the Néel temperature [181,312]. The susceptibility increases with temperature of heat-treatment [121,181,249]. These phenomena, which have been termed "pseudoferromagnetism", usually disappear in solution [312,341], as does also the broad (hundreds of oersteds) ESR signal¶ (occasionally observed [118,187,199,227,312,342]), which becomes even broader at low temperatures and frequently corresponds to an unacceptably high number of paramagnetic centres (up to 10^{22} per gramme, or upwards of 10 per monomer unit)[342]. Similar effects have been reported for nucleic acids and their complexes with proteins [338,343,344]. It was pointed out that the compensation effect in electrical conduction should not occur in substances showing these properties [334,335].

Attempts were immediately made to relate this unusual behaviour of organic substances to the specific features of conjugated polymeric systems: in particular, to the collective interactions arising in π-electron systems of this type as a result of a particular ordered structure [29,312], or to the formation of charge-transfer complexes [338,341]. However,

† With *p*-type polyethylene subjected to radiation–thermal treatment, the specific resistance ρ and E_σ were both found to decrease [269] in the presence of O_2.

‡ Myl'nikov [259] explains the suppression of dark conduction and photoconduction caused by O_2 adsorption on a *p*-type polymer by postulating that oxygen gives rise to carrier recombination centres on the surface.

§ The increase in resistance is sometimes due to removal of impurities by the heat-treatment [129,184,227].

¶ Instances have been reported, however, in which the positive susceptibility [339] and the broad ESR signal [342] persist in solution.

Dorfman has suggested that these properties cannot be ascribed to organic structures[345,346], and must be due to contamination (by iron compounds, in particular), as has on occasions been demonstrated experimentally[203,347,348]. On the other hand, and in keeping with the view that these phenomena are not trivial in origin, positive susceptibility has been observed for polymers prepared under high-purity conditions[162,181], and the concentration of ferromagnetic impurity present has been shown to be clearly insufficient to explain the observed effects[341,349]. Hence, Blyumenfel'd believes[349] that, although the specific pseudoferromagnetic behaviour of organic compounds is associated with the presence of iron, nevertheless it is due either to a special state of the system, in which all five $3d$-electrons of the Fe^{3+} ion take part in domain formation (as in a new type of ferrite), or alternatively the behaviour is due to specific exchange interactions between the paramagnetic iron ions through the conjugated organic structure. The question of whether the static paramagnetism and the broad ESR lines are trivial in origin is still not finally settled (in contrast to the nature of the narrow ESR signal, see Section III).

The magnetic susceptibility method is used in the study of chelate polymers with paramagnetic ions to establish the structure of the chelate link[22,252,255,256] and to reveal exchange interactions through the conjugated system[224]. In the latter case, use is made also of changes in the ESR signal for chelates with metals whose ions give resonance absorption[224,263].

4. Narrow-Line ESR

Practically all polymers with conjugated bonds give a characteristic narrow ESR signal either as prepared or after further heat-treatment. As with other classes of organic semiconductors, the absorption line is a singlet†, characterised by a g-factor close to the free-electron value ($g \simeq 2.00$), of small width (ΔH from 0.5 to 15, and rarely up to 50 oersteds), and with a relatively high concentration of unpaired spins ($N \simeq 10^{16}$–10^{21} per gramme, or 1 spin per 10–10^6 molecules)‡. The temperature dependence of the signal intensity usually follows Curie's law[3,112,143,161,162,182,183,190,198,251,273], although temperature-independent signals have been reported[68,250,269]§. The width of the signal does not vary with the measurement temperature[56,112,198,251]. The signal invariably persists when the material is dissolved[3,56,68,74,83,105,185,306,312]¶, and in many cases the shape remains unchanged and the intensity decreases in proportion when the solution is diluted[3,68,74,195].

The ESR signal suffers irreversible changes as a result of heat-treatment of the polymers. The concentration of unpaired spins N increases with temperature[3,105,160,162,170,182,205,246] up to a maximum at 600–700° (for measurements made in a vacuum)[47,269,273] and then gradually falls as the temperature is raised still further, but the signal is not completely lost at 900° and even above 1000°,[85,273,275]. The line width ΔH retains its original value of 4–8 oersteds up to heat-treatment temperatures of 400–500°,[47,85,269] but it goes through a minimum (for the case of vacuum measurements) at 500–700° which can be as low as 0.5 oersted, and further increase in pyrolysis temperature broadens the signal (upwards of 10 oersteds).

Oxygen does not usually affect the ESR signal of polymers which have not been heated above 300–400°,[85,269] but a decrease in N is occasionally observed even for low-temperature specimens[44,103,203]. After heating above 300°, oxygen is found to have an effect on ΔH: measurements in air do not show a minimum and ΔH remains constant up to heat-treatment temperatures of 500–600°, beyond which the line becomes wider (as in the vacuum measurements)[47,85,123,205,269]. Bakh and coworkers[269,275] consider that the minimum in ΔH observed after heat-treatment at 500–700° is only apparent, and due to inadequate pumping off of O_2, since after thorough degassing ΔH has its minimum value (0.5 oersted) even for the lowest baking temperatures. Line broadening in the presence of oxygen probably arises from the local magnetic fields generated by the adsorbed O_2 molecules, which alter the value of the g-factor for different regions[279]. The effect of O_2 on the concentration N of unpaired spins becomes appreciable after heating the polymer above 500°, and produces a slight shift of the maximum towards lower heat-treatment temperatures (500–600° instead of 600–700°)† and a sharp decrease in N at higher temperatures. In polymers heated to 650–800° the ESR signal vanishes when measured in air[47,85,121,269], whereas with samples heated at higher temperatures[275] and some other polymeric samples[74] (measurements *in vacuo*) there is an increase in N on admitting O_2, due to the formation of charge-transfer complexes with oxygen (see p. 780). All these changes in the ESR signal are similar, on the whole, to the phenomena observed in charcoals[12]. We should stress that the differences between carbons and heat-treated polymers are arbitrary in a number of respects (see, for example, Ubbelohde[22]), and therefore it is quite likely that the ESR signal found in low-temperature charcoals is often caused not by broken bonds[12,351] but by the factors which operate in polymers with conjugated bonds and other organic semiconductors (see Sections IV and V).

The shape of the ESR line can vary from the Gaussian to the Lorentz form, depending on the conditions of pre-treatment of the polymer, the measurement temperature, and adsorption[56,68,74,123,153,195,198,269,273,275,279,293]. For low-temperature samples and low measurement temperatures the signal is of Gaussian or intermediate form, but, on raising the heat-treatment or the measurement temperature, the line gradually acquires Lorentz character[123,153,269,275]. This is consistent with stronger exchange interactions between the paramagnetic centres as the number and size of the conjugated regions are increased. Adsorbed oxygen enhances the Lorentz character of the signal by contributing to electron exchange[195,296], in keeping with the strong influence of O_2 on the electrical conductivity of low-temperature polymers[95,269] and with the analogous effect of iodine adsorption[198,270,271].

In most cases the ESR signal is a symmetric singlet, but occasionally some asymmetry is reported: with low-

† Double, or more complex, signals have been observed[105,109,161,164,190], and ascribed to isolated radicals[105]. After heating, the signal becomes a normal singlet. Hyperfine structure is sometimes revealed by measurements in solutions[56,185].

‡ Chelate polymers can give an ESR signal either because of the presence of a paramagnetic metal ion (broad line) or for reasons common to all organic semiconductors (narrow line)[224,245,250,251].

§ A decrease in the concentration of unpaired spins on cooling the polymer has been reported only once[198], and ascribed to the formation of a stable charge-transfer complex with iodine, or to the iron polychelate complex[250].

¶ Reversible loss of signal on dissolution has been reported for aniline black[203] and for polymeric charge-transfer complexes[293], as commonly observed with low-molecular organic semiconductors[350]

† Under some conditions the maximum in N can be found at very much lower temperatures[121,191].

-temperature polymers, the asymmetry arises from the ready saturation[44,56,227,279,293,306,352] due to the large spin--lattice relaxation time (10^{-4}–10^{-5} s),[49,352] but, with the highly conducting, high-temperature polymers, the asymmetry is associated with the skin effect or with the asymmetry of the g-factor[273,275]. Saturation is less marked after adsorption of oxygen[68,74,279,293] which favours spin–lattice interaction.

The ESR signal in polymers is very interesting from the point of view of their catalytic activity, since it has been possible in some cases to demonstrate a direct correlation between catalysis and the concentration of unpaired spins[39–41]. In this connection we should mention a series of papers by Berlin and coworkers on the so called local activation[41,353–356]. According to this concept, the paramagnetic centres present in compounds with conjugated bonds, and responsible for the special magnetic behaviour of materials of this type‡, excite (or activate) the neighbouring molecules and thus give rise to catalytic activity, fluorescence, dark conduction and photoconduction, and other specific properties of organic semiconductors. The mechanism of this effect evidently involves perturbation of the electronic shells of the system under the influence of the local magnetic centres, and consequently an increased probability of reaction occurring via the excited triplet state, i.e. with a lower activation energy[354,356].

III. NATURE OF THE NARROW-LINE ESR

Generally speaking, the following basic factors, which can cause the appearance of an ESR signal in organic structures of the type under discussion, are significant: (a) inorganic paramagnetic impurities; (b) organic radicals, arising either in the course of polymerisation ("trapped radicals") or during thermal degradation of the polymers ("broken bonds"); (c) stabilised double radicals, formed by the Berlin mechanism (see below); (d) the transition of molecules to the triplet state, whose level can be so low in highly conjugated systems as to be readily populated even at room temperature ($^3E_1 \simeq kT$), or even become the ground state ($^3E_1 < kT$); (e) the appearance of polar states as a result of charge-transfer processes — in particular, the formation of charge-transfer complexes; (f) the signal from quasi-free current carriers.

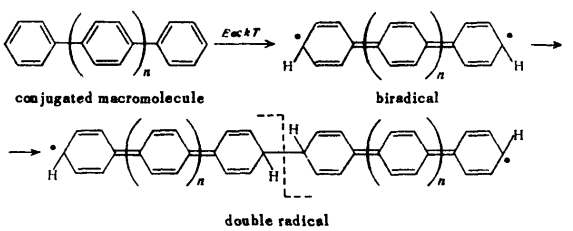
The narrow ESR signal in polymers was originally assigned to the properties of an individual highly conjugated molecule[24,29,228], and ascribed to a specific phenomenon (the appearance of some measure of unpaired character in the π-electron system at a particular stage of conjugation[29,63,245]). This interpretation is consistent with the narrowness of the line, with the dependence of the signal on the degree of conjugation in the molecule[45,84,123,176,191,306,352], with the correlation between changes in N and colour[23,175], and with the fact that the signal persists in solutions. However, many contradictions were soon discovered. Although instances of monotonic variation of the concentration N of unpaired spins with molecular weight were reported[191,207], in other cases there was no correlation between these parameters[56,84]. The observed proportionality between N and the molecular weight[68,74] cannot be reconciled on the basis of the above ideas with the fact that the length of the conjugated system does not increase with molecular weight[69]. The limited degree of delocalisation, which extends over no more than 2–7 monomer units[56,68,74,123], has been demonstrated on numerous occasions.

Furthermore, the character of the observed ESR signal did not provide an explanation of the appearance of paramagnetic centres in terms of other possible mechanisms of intramolecular excitation: either by thermal activation of the singlet–triplet transition (since the intensity varies according to Curie's law, i.e. N is independent of temperature) or due to the fact that the triplet state becomes the ground state (since the concentration of paramagnetic centres is always less than one per molecule)§.

This situation has given rise to suspicions that the ESR signal in polymers is due to impurities. However, as in the case of low-molecular organic semiconductors, we can dismiss trivial paramagnetic contaminations because: (a) all paramagnetic ions give a signal of significantly greater width[357]¶; (b) there is no analogy among inorganic para- and ferro-magnetics to irreversible temperature changes in the signal (see p. 778); (c) the signal often appears only after heating[48,168,170,323] or low-temperature carbonisation[306,340,352]; (d) the behaviour of the signal can be correlated with the colour of the material and with conjugation in the molecule[45,84,122,123,191]; (e) the signal is strongly affected by adsorption of O_2 and other substances.

At the moment, only two approaches offer a satisfactory treatment of the basic features of the paramagnetic behaviour of polymers with conjugated bonds and other organic semiconductors: Berlin's ideas on stable double radicals and the concept of charge transfer proposed by Blyumenfel'd and Benderskii.

According to the views of Berlin[15,49,84,162,359], centres which appear in the fractions of highest molecular weight are responsible for the ESR signal. Macromolecules in which a sufficient degree of conjugation is achieved (irrespectively of whether the polymerisation mechanism was radical, ionic, or molecular) can pass into the triplet state even at ordinary temperatures. The interaction between two or several such excited biradicals, termed quasi-radical polymerisation, gives a stable double radical according to the scheme



The unpaired electrons of this double radical do not interact, and do not recombine, because a mutually coplanar arrangement of the individual conjugated blocks is sterically impossible. The resulting molecular paramagnetic centres are additionally stabilised by the formation of charge-transfer complexes between the double radical and the neighbouring molecules: this, in turn, favours the excitation of these molecules to the triplet state by the local-activation mechanism (see p. 779). This explanation of the paramagnetism of polymers with conjugated bonds

‡ The nature of the paramagnetic centres is discussed in Section III.

§ This is true also of the ESR signal ascribed to the triplet state of nitrogen[182,183].

¶ Even in chelate compounds in which exchange interactions take place through organic structures[358].

evidently lacks generality, since an ESR signal can be observed also in systems where the formation of extensive conjugation chains is improbable† [122].

The hypothesis that the ESR signal in organic semiconductors is due to polar states involving charge transfer was put forward and developed in a series of papers by Blyumenfel'd and Benderskii [68,69,306,360,361]. At present, these ideas perhaps offer a more satisfactory explanation of the peculiarities of the ESR signal of low-temperature polymers [75,83,85,122,123,162,196,198,203,205,293] and of other classes of organic semiconductors [12,309,359,362,363]. According to this model, the low ionisation potential of conjugated systems assists the formation of local centres of the radical-ion type in the solid structure. The charge transfer which accompanies the appearance of these localised polar states can occur either between two neighbouring molecules, when the charge transfer is assisted by the shorter intermolecular distance, and the resulting charge-transfer complex is treated as a structural defect of the lattice, or it can involve charge capture by more remote molecules, traps, crystal defects, etc. ‡

The formation of polar states involving charge transfer is assisted by: (1) the presence of a sufficiently extensive conjugated π-electron system, which ensures high polarisability and ready ionisation of the molecules; (2) polydispersity, which produces differences in electron affinity and ionisation potential between the molecules; (3) polarity of the molecules, and in particular the presence of nitrogen atoms (which also increases the electronic heterogeneity of the system); (4) disorder and structural defects in the material as a whole, which provide the best conditions for local interactions between molecules and for the formation of traps. In the case of polymers, a special role is played by polydisperseness (as pointed out by Dulov [122] and Boguslavskii [200]), and by disorder, as evidenced by the fact that amorphous polymers are often better semiconductors than crystalline polymers [61,122,168,175]. This approach explains the contradictions pointed out on p. 779, since the formation of polar states is determined both by properties of the molecule (conjugation), and also factors less easy to characterise, such as polydispersity and structural disorder.

It should be noted that in some cases the ESR signal can arise from well known, alternative causes. In particular, the ESR signal resulting from charge-transfer complexes formed by electron transfer between a compound with conjugated bonds and an adsorbed molecule of oxygen [74,195,198,275,362,364-366] or some other molecule (see p. 774) has been specially discussed by various workers. The ESR signals sometimes observed from common radicals formed during the synthesis and trapped in the polymer structure, or from radicals of the broken bond type appearing, for example, during thermal breakdown of the polymer [105,273,367], are easily distinguished by their behaviour, since they should disappear irreversibly on dissolution or moderate heating.

In many cases (for example, in polymers heated above 900° [273] or even at lower temperatures [143]) a narrow ESR signal caused by the current carriers can be detected, similar to the signal observed in individual low-molecular charge-transfer complexes with strong binding [368-370]. Benderskii and others were able to isolate a narrow signal from photo-induced carriers in dyes, and showed that its behaviour differs from that of the broader signal associated with local paramagnetic centres [371].

IV. ELECTRICAL CONDUCTION MECHANISM

A clear description of the current-carrying processes in organic semiconductors, and particularly in polymers, is perhaps the most serious outstanding problem in the study of these interesting materials. Any mechanism proposed must explain a number of specific features of the electronic behaviour of these compounds which are now well established. The following are the most important peculiarities.

1. Electronic inhomogeneity. Measurements by various methods (a.c. measurements [200,237,243,269], studies of current noise [141] and of the effect of the adsorption of iodine [161] and of air [135], and other investigations [47,122,227,242,275]) lead to the firm conclusion that all polymers consist of discrete conducting regions (very probably, strongly conjugated or condensed regions) separated by poorly conducting (dielectric) regions evidently consisting of a disordered structure of polymer molecules (see p. 775, 776).

2. Nature of the reversible temperature dependence of the thermo-e.m.f. In most cases the thermoelectric power α is either practically independent of temperature [100,125,127,132,143,145,176,200,214,231,269,270,272] or increases at higher temperatures [100,143,145,154,176,212,229]. This suggests that the temperature variation of α and σ is the result of a change in carrier mobility at constant carrier concentration, since theory predicts a weak (logarithmic) increase of α with temperature for this type of mechanism (degenerate conductor) [14,328]:

$$\alpha = \frac{k}{e}\left[A + \ln \frac{2(2\pi m^* kT)^{3/2}}{h^3 n}\right],$$

where A is a constant which depends on the electron scattering mechanism, m^* and n are the effective mass and the concentration of the current carriers respectively, k and h are Boltzmann's and Planck's constants, and T is the absolute temperature.

When the changes in α and σ with temperature arise mainly from an exponential increase in the carrier concentration, the theory requires that α decreases with increase in temperature, in direct proportion to $1/T$: [14,328]

$$\alpha = \frac{k}{e}\left(A' + \frac{E_\sigma}{kT}\right).$$

Some polymers have shown a decrease of α with temperature [64,132,143,145,154,170,172] but the observed effect is not usually large enough to justify ascribing it to the influence of carrier concentration [64,145,172].

3. Very low mobility of charge carriers. Attempted measurements of the carrier mobility in polymers from the Hall effect have usually proved unsuccessful [48,140,157,200,225,229]. This suggests that the mobility does not exceed 0.005–0.01 $cm^2 V^{-1} s^{-1}$. Only in two cases have

† Also, a recent tentative calculation [75] shows, that the degree of polymerisation achieved (in particular) in poly(phenylacetylene) is apparently sufficient to allow transition of the molecule to the triplet state.

‡ Complexes involving partial charge-transfer can be formed [288]. Localised centres of this type do not, of course, give an ESR signal.

these measurements given positive results: poly(acenequinone) radicals gave the very low value [172,216] 0.04 $cm^2 \times \times V^{-1} s^{-1}$, and an unexpectedly high mobility (2.5–10 $cm^2 \times \times V^{-1} s^{-1}$) was observed in poly(copper phthalocyanine). However, the Hall effect measurement for the latter polymer could not be reproduced§ [225,229], and a measurement of mobility from the effect of O_2 adsorption on σ gave very much lower values [229]. Low mobility values in the polymers have been deduced also from ESR data (10^{-1}–10^{-3} $cm^2 V^{-1} s^{-1}$, [64,68,172,372]) from a.c. measurements (10^{-3}–10^{-5} $cm^2 V^{-1} s^{-1}$, [271]) and from calculations based on the band model (10^{-2}–10^{-7} $cm^2 V^{-1} s^{-1}$ [100,145,201,214]). Evidently, higher mobilities can be obtained only when the influence of the dielectric interlayers is eliminated: values of 1.4–100 $cm^2 V^{-1} s^{-1}$ have been reported [229,230,271,273,284,373]. Positive holes are usually found to be more mobile than electrons [100,140,201,208], but calculations sometimes yield the opposite result [261]. The concentrations of current carriers corresponding to the low mobilities listed above amount to 10^{12}–10^{17} cm^{-3}. [172,201,214,216,230,372]

All these special features are best explained in terms of the hopping mechanism of conduction [14,16,17,125,127,128,145,200,214,237,238,243,318], according to which current is obtained by activated hops of the carriers, over the dielectric barriers created by the disordered (non-conjugated) structures, from one polyconjugated region to the next. Under these conditions, a rise in temperature does not alter the number of effective carriers present in the polyconjugated regions (provided of course that irreversible pyrolytic processes are excluded), but it increases the probability of a jump, i.e. the mobility. As shown by the theoretical work of Klinger [374] and of Lang and Firsov [375], the hopping mechanism is the most probable in materials of low carrier mobility, in which the current is carried by small polarons and difficulties arise in the measurement of the Hall effect. This mechanism explains also the characteristic temperature variation of α of the majority of polymers, and the results obtained, in measurements with a.c. [200,237,238], with stretching and compression of a heat-treated polymer [128].

According to the band mechanism [117,154,172,328], the intermolecular π-electron interactions give rise to a conduction band which is common to the whole volume of the polymer, and in which the concentration of carriers depends on the energy needed to extract an electron from the π-conjugated system and transfer it to the quasi-free, conducting state. In other words, the carrier concentration is determined by the width of the forbidden gap, and increases with temperature. From the point of view of the band theory, a low mobility is the result of narrow bands (large effective carrier mass). However, this mechanism is inapplicable to the majority of polymers because it is inconsistent with the temperature variation of α [64,71,100,125,127,132,143,145,176,212,214,229,231,269,270,272] and with the extremely low mobility, corresponding to an improbably small mean free path (less than 1 Å) [17,140,214,230] and to unacceptably large effective masses of carriers [140]. Furthermore, the band model is particularly improbable for polymeric materials, which usually lack a crystalline structure [376] (although calculation has shown [377,378] that strict ordering is probably unnecessary to give rise to an electronic band structure in polymers). Nevertheless, there are cases, such as when the mobility is greater than 1 $cm^2 V^{-1} s^{-1}$, or when α decreases with temperature (see below for the strong carrier–carrier interaction which sometimes arises under these conditions, giving rise to pseudometallic conduction [372]), and also in photoconduction processes [48], where the band mechanism can be applied with some reservations [143,183]¶.

The tunnel mechanism [7,64,78,135,136,158,232,248] assumes that the true activation energy for conduction E_σ (ignoring the effects of adsorption, cross-linking, etc.) is determined by the energy needed to transfer an electron to an excited level in the molecule, so that E_σ in polymers with conjugated bonds should be small and tend to vanish as the degree of conjugation in the macromolecule is increased. The magnitude of the conductivity is limited by the probability of non-activated intermolecular tunnelling of the electrons, which is itself largely determined by the thickness and shape of the intermolecular barriers. The effectiveness of tunnelling transitions is proportional to the concentration of electrons in excited levels, itself an exponentially increasing function of temperature. With polymers, in contrast to low-molecular organic semiconductors and individual charge-transfer complexes [14], it is difficult to confirm the correctness of the tunnel mechanism by comparing E_σ with optical data [98,99], but is has been done [64]. Some workers [232] have postulated a tunnel mechanism on the grounds that the experimentally observed curve of activation energy *versus* the degree of crystallinity (which determines the shape of the barriers) agreed with the calculated curve. Others, however, have adopted this mechanism without sufficiently convincing evidence [78,135,136,248]. The tunnel mechanism seems hardly likely to be generally applicable to polymers with conjugated bonds, because the objections raised against it, even in the context of low-molecular organic semiconductors (to which it can be applied with much better justification [376,383]), are very cogent in the case of polymers, in particular, the much lower probability of the tunnel mechanism than of the hopping mechanism in substances with a low carrier mobility [375]. It is also interesting that the very small activation energies for carrier generation within the conjugated region (0.1 eV approximately) have been confirmed experimentally by a.c. measurements [268], but these same measurements have shown that the rate of the d.c. conduction process is limited by a stage attended by a considerable activation energy (of the order of 1.0 eV), i.e. probably by barrier jumps between conjugated regions.

Thus, the hopping mechanism appears to be the most plausible for the majority of typical polymeric semiconductors†. However, in some groups of polymers the electrical conduction is known to arise by different mechanisms. In particular, when the mobility exceeds 10 $cm^2 V^{-1} s^{-1}$ (i.e. for high-temperature samples [85,273], for compositions

§ The high mobilities in this case can probably be ascribed to the participation of the *d*-orbitals of the copper atom under favourable steric disposition of the molecules, as has been demonstrated for the monomeric copper phthalocyanine [266].

¶ It may not be out of place to point out that recent Hall effect and conductivity measurements on inorganic semiconductors (NiO and CoO) have shown that the band model is applicable to these oxides [379,380], although the hopping mechanism had been previously postulated on account of their low mobility [381]. Some recent calculations [382] of a number of electrical parameters of organic semiconductors have given grounds for retaining the band concepts for systems of this type.

† An alternative view, recently put forward, is that the electrical behaviour of semiconducting polymers is determined by the superposition of two activated processes: changes in the concentration of current carriers and changes in their mobility [175,242], as had already been proposed for organic semiconductors of low molecular weight [383,384].

with a high metal content[231], or when strong charge-transfer complexes are formed with polymers[271]), and also when α is found to decrease steeply with temperature[132], the electrical conduction is probably quasi-metallic as a result of strong electronic interactions in the polymer. Under these conditions the carrier concentration can be appreciably higher than normal (up to 10^{19} cm^{-3}).[143,273]

The chelate polymers form another special group, in which metal ions play an essential role. The specific features of the electrical properties of polychelates have been explained by invoking the ligand field theory[254], the resonance of structures involving a metal[265], or (by analogy with ferrites) a mechanism in which the electronic jumps depend on the variable valence of a metal ion[265].

V. RELATIONSHIP BETWEEN ELECTRICAL AND MAGNETIC PHENOMENA AND GENERAL THEORIES OF SPECIFIC EFFECTS IN ORGANIC SEMICONDUCTORS

A superficial comparison might lead to the conclusion that in general there is no correlation between the electrical conductivity σ and the paramagnetism of polymers with conjugated bonds. In the first instance, the irreversible temperature changes in σ and in the concentration of unpaired spins N, which occur during pyrolysis, are different (except after low-temperature heating, when the changes are in the same sense): σ increases continuously, whereas N goes through a maximum (see p. 777 and 778). But even when the changes are monotonic, an increase in σ by many orders of magnitude corresponds to an increase in N by a factor of only several tens or hundreds[64,122,214]. Secondly, the reversible temperature variation of the width of the ESR signal, in accordance with Curie's law, suggests that N stays constant, whereas σ has a positive temperature coefficient (see p. 775 and 778). Thirdly, in most cases N is greater than n (the concentration of current carriers)[64,143,214,273]. (See also Tobin's calculation[372] based on the results of Hatano and coworkers[63]; see p. 778 and 780.)

However, a deeper study of the problem reveals a correlation between the electrical and magnetic properties.

(a) Despite the fact that in most cases there is no quantitative correspondence between N and n (i.e. that the ESR signal is not, in fact, given by the current carriers), a distinct correlation is very often observed between changes in N and changes in electrical properties on heating in the low-temperature region[85,170,205,227,269], during chemical reactions[45,111], as the degree of crystallinity is increased[63], on changing the extent of conjugation[64,122,177], and for photo-induced electrical and paramagnetic characteristics[52,69]. In some groups of related polymers a direct proportionality between N and $\log\sigma$ has even been observed[122,214].

(b) The existence of a close association between the semiconductor properties and the ESR signal is suggested also: firstly, by the temperature independence of both N (Curie's law) and n[143,273] (see p. 780), and, secondly, by the success achieved in explaining the electrical behaviour of polymers by applying the ideas of polar states and charge-transfer complexes (see p 779) and of local activity centres (p. 778). The studies of polymers treated with halogens[174,198,205,211,289] provide the best example of this, since in every case the authors were able to correlate the improvement in electrical characteristics with the formation of charge-transfer complexes. The same conclusion probably applies in every other reported case of decrease in resistance and in activation energy E_σ following introduction of halogens[17,261,290] or metal salts[48,51] into the polymers. Karpacheva[174] obtained a direct demonstration that the maximum concentration of paramagnetic centres in the bromine and iodine complexes of polymeric Schiff's bases occurs at the same composition as the minimum activation energy for conduction E_σ and minimum resistance. A monotonic increase in photoelectric activity with concentration of paramagnetic centres was observed in a study of the local activation effect[69,356,385]. Further evidence for a close link between electrical conductivity and charge-transfer complexes is provided by the decrease in E_σ with increasing polarity of the molecules[314] (see p. 780).

(c) In polymers which have been heated to sufficiently high temperatures the concentration n of current carriers can become equal to the concentration N of unpaired spins[143,274]. Under these conditions the strong electronic interactions give rise to quasi-metallic conduction (see p. 781), and the ESR signal is obviously produced by the conduction electrons[143,273]‡. On further raising the pyrolysis temperature, the increasingly strong electronic interactions can lower the effective concentration of unpaired spins (and even cause the ESR signal to disappear altogether, see p. 778), so that N becomes smaller than n.

Thus, we are forced to the conclusion that the electrical and magnetic properties of polymers are by their very nature closely interrelated, although the relationship is a complex one, and can be masked by various subsidiary phenomena.

Not surprisingly, in view of the fact that comparison of the properties of other groups of organic semiconductors has led to a similar conclusion[361,368,369,385,386], attempts have recently been made to evolve generalised theories of the electrical and magnetic effects in organic semiconductors. We refer first and foremost to Blyumenfel'd and Benderskii's[360,361,378] theory of polar states already mentioned above (p. 779), which is primarily concerned with the formation and dissociation processes of local paramagnetic centres, and to Pohl's ion–exciton model[17], which deals mainly with the mechanism of current transport§. The local activation concept developed by Berlin and coworkers also aims to unify the nature of electrical and magnetic phenomena in organic semiconductors, and has already been mentioned on p. 778 and 779.

Blyumenfel'd and Benderskii consider that the electrical and magnetic properties of organic semiconductors are determined by the activation energy of a polar state within the crystal, i.e. by the concentration and also by the nature of the local paramagnetic centres, consisting of defects in the crystal structure. Generation of charge carriers

‡ This mechanism of the generation of an ESR signal is similar to that demonstrated by Wagoner for high-temperature charcoals[386], but our polymers (unlike the latter materials) show a strong variation of signal intensity (i.e. of N) with O_2 adsorption, which has no effect, however, on the electrical conductivity[85,269]. Hence, it is doubtful whether the ESR signal in polymers which have been heated only a little above 800° is in fact caused by conduction electrons. These considerations have led to the suggestion[85] that electrical conductivity arises not only from unpaired electrons, but also from delocalised, strongly interacting electrons (or holes) which do not give an ESR signal.

§ Pohl's discussion deals specifically with ionic conduction, but his arguments are equally applicable to current transport by electrons and holes, which has been proved to exist in organic semiconductors (see p.775 and Ref. 5).

occurs by dissociation of the polar state by the normal exciton mechanisms[8,387]. For very weak intermolecular interactions, the levels of the polar states lie well above the ground state of the system, and therefore the concentration of polar (paramagnetic) centres is very small and the materials should be diamagnetic and insulating. In compounds of this type, which includes low-molecular organic semiconductors and possibly also poorly conducting polymers, the ESR signal can arise only from charge-transfer complexes, formed by the reaction between molecules of the main constituent and easily ionised non-paramagnetic impurities (in particular, high-molecular fractions). As the interactions in the solid become stronger, the levels of the polar states shift downwards, with an increase in the concentration of intrinsic paramagnetic centres able to generate an ESR signal as a result of electronic transitions between molecules of the matrix. In these compounds (among which we classify some strong, individual charge-transfer complexes and many highly conducting polymers) we expect to find a relationship between electrical and paramagnetic characteristics. When the intermolecular bonds are strong enough, the levels of the polar states can become practically indistinguishable from the unexcited level, and in this case the paramagnetic state becomes the ground state of the system. Substances of this kind should exhibit a characteristically temperature-independent paramagnetism and high conductivity, like the better individual charge-transfer complexes based on tetracyanoquinodimethane[389]. However, when the levels of the polar states are shifted even lower, the radical-ions formed by electron transfer can behave as independent paramagnetic centres (Curie's law), and the resistance should rise again (as in ionic crystals); this situation may exist in the charge-transfer complexes involving halogenoquinones[388,390]¶. Unfortunately, the theory of polar states, though it offers a satisfactory description of the paramagnetism of organic semiconductors, does not underline sufficiently the specific aspects of the conduction mechanism, since it examines charge transfer essentially from the standpoint of the exciton band model.

According to Pohl, whose approach is based on the concept of ion pairs[391], the molecules of an organic semiconductor form chains (or groups) of ion–exciton complexes of the type $(M^+M^-)\ (M^+M^-)\ \ldots\ (M^+M^-)_x$ in which electronic excitation and electron transfer are greatly facilitated by the strong exciton–exciton and ion–exciton interactions. Hence the steady-state concentration of excited electrons in the system can be quite high, and this will increase the probability of electron exchange between these polymeric forms of excitons by the activated jump mechanism. On the whole, this model describes satisfactorily the special features of the electrical behaviour of organic semiconductors, but unfortunately Pohl does not consider the concrete mechanisms of intermolecular interactions in molecules of various types, nor does he accord special attention to the properties of exciton–ion complexes as paramagnetic centres in organic semiconductors.

Although the nature of the special electrical, magnetic, catalytic, and other properties of organic semiconductors is still far from clear, there can be no doubt that in the last few years this class of organic compounds has attracted exceptional interest from physicists and theoretical chemists. Thus, we may hope that the next few years will witness the appearance of a unified theory of the electronic effects in organic semiconductors, which will make it possible to understand the true nature of the specific properties of these remarkable compounds and to control those properties by rational methods.

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The above review of the experimental results for and of the theoretical models of semiconducting polymers, in conjunction with published work on other groups of organic semiconductors which could not be discussed here, justifies the following conclusions.

1. All organic semiconductors (polymers with conjugated bonds, one-component conjugated systems of low molecular weight, charge-transfer complexes, biological materials, and charcoals) have in common a group of special properties which distinguishes them from most of the ordinary organic compounds: this is particularly true of their electrical, magnetic, catalytic, and also some other characteristics.

2. The peculiar behaviour of organic semiconductors arises, on the one hand, from the presence of conjugated π-bond systems in their molecules, and, on the other hand, from specific features of the solid-state structure of these compounds (in the case of polymers the presence of electrically conducting highly conjugated regions separated by dielectric layers).

3. Although a unified interpretation of the nature of the paramagnetism in organic semiconductors is still lacking, we can now assert that the most common cause of a narrow ESR signal in these materials is the presence of paramagnetic polar states (in particular, charge-transfer complexes) whose formation is very considerably assisted by the properties of the system of conjugated π-bonds. A special case is provided by charge-transfer complexes involving adsorbed molecules of oxygen, or charge-transfer complexes into which molecules of halogens or of some other materials have been introduced.

4. The most satisfactory explanation of the special electrical behaviour of organic semiconductors relies on the activated hopping mechanism, although in some cases (compounds of low molecular weight, and individual charge-transfer complexes) the band model also can be applied.

5. The problem of the basic common origin of electrical and paramagnetic phenomena in organic semiconductors is not finally settled, but in many instances we have convincing proof of a correlation between these properties, and some of the theoretical concepts already put forward may lead to a unified explanation of the special electrical and magnetic behaviour of organic semiconductors.

¶ Admittedly, it becomes difficult in the latter case (level of polar states below ground level) to explain the fact that the experimentally determined concentration of the paramagnetic form in organic semiconductors is almost invariably less than 100%.

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CHEMISTRY OF DIFLUORAMINE

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1. INTRODUCTION

Until recently there had been very little investigation of difluoramine HNF_2. The main publications about it [1-3] related predominantly to its physical properties and to the history of the methods of its preparation, whereas its chemical properties remained almost uninvestigated, owing to the extreme hazard in working with it.

Of the three theoretically conceivable compounds in the series of fluoro-substituted ammonias only two are known at present: nitrogen trifluoride NF_3 and difluoramine HNF_2. The physical and chemical properties of nitrogen trifluoride are sufficiently well known [1-3]. The fluorine–nitrogen bond in NF_3 has a polar character, which determines the shift in the electron density towards the base of the regular pyramid with the nitrogen atom at the apex and the fluorine atoms in the base. It is also generally known that the ammonia molecule is extremely nucleophilic, owing to the unshared pair of electrons at the nitrogen atom. As the hydrogen atoms in it are replaced by fluorine atoms, an ever-increasing deficit in electron density is produced at the nitrogen atom (in compensation for which the electron lone pair of the nitrogen should play an ever-increasing part). Hence owing to the powerful inductive influence of the fluorine atoms there is a significant deactivation of this electron pair, increasing with the degree of substitution, and a sharp fall in the basic properties of the fluoro-substituted ammonias. This deactivation should be maximal in the nitrogen trifluoride molecule.

The same distribution of electron density along each nitrogen–fluorine bond in the NF_3 molecule and the almost complete absence of nucleophilic properties at the nitrogen atom confers on nitrogen trifluoride a high chemical inertness at temperatures up to 300–400° and explains the exclusively homolytic cleavage of the bonds under more intensive thermal action. Therefore all the reactions in which nitrogen trifluoride is at present known to participate are usually pyrolytic and have a radical character.

A feature of the structure of the difluoramine molecule gives it a reactivity which indicates the high degree of polarisation of the nitrogen–hydrogen bond $\overset{\delta+}{H}-\overset{\delta-}{N}F_2$, which under suitable conditions is capable of heterolysis with the formation of the difluoramide anion NF_2^-.

If the tervalent nitrogen atom in the ammonia molecule is considered to be in a reduced state and the tervalent nitrogen atom in nitrogen trifluoride is in an oxidised state, then the difluoramine molecule undergoes both oxidation and reduction.

Hence the difluoramine molecule, by allotting a rather active long pair of electrons to the nitrogen atom and with a hydrogen atom capable of loss as a proton, exhibits an amphoteric nature. The presence in it of an N–H bond capable of being oxidised, and of an N–F bond capable of being reduced, confers on it the dual character of reactivity in redox changes. The combination of such a variety of properties is usually responsible for the diversity of the chemical reactions in which difluoramine participates.

2. PHYSICAL PROPERTIES AND STRUCTURE OF THE DIFLUORAMINE MOLECULE

Difluoramine is a colourless gas with a characteristic sharp odour, reminiscent of the odour of nitrogen oxides, liquefying below -23° into a transparent, colourless, mobile liquid. The most important physical properties of difluoramine have been studied recently by Lawton and Weber [4,5] and by Kennedy and Colburn [6].

The microwave spectra of difluoramine and deuterated difluoramine have been investigated [7]. The HNF_2 molecule is characterised by the following parameters [7]:

length of nitrogen–fluorine bond	$r_{N-F} = 1.400 \pm 0.002$ Å,
length of nitrogen–hydrogen bond	$r_{N-H} = 1.026 \pm 0.002$ Å,
F–N–F bond angle	102.9°,
H–N–F bond angle	99.8° ± 0.2°.

The difluoramine molecule is thus an irregular triangular pyramid with the nitrogen atom at the apex.

The dissociation energy of the nitrogen–hydrogen bond in difluoramine $D(F_2N-H)$ is 72.5 kcal. [8]

The dipole moment of the HNF_2 molecule is 1.93 D, and its vector is directed at an angle of 19° to the direction of the nitrogen–hydrogen bond. This agrees well with the hypothesis of polarisation of the nitrogen–hydrogen bond and the tendency of difluoramine to dissociate according to the equation:

$$HNF_2 \rightleftharpoons H^+ + NF_2^-.$$

The infrared spectrum of gaseous difluoramine in the region 250–4000 cm^{-1} has been investigated; it includes strong doublets at 7.0, 7.8, and 10.2 μm and a triplet at 11.2 μm. [3]

The proton-NMR spectrum consists of a triplet, as should follow from proton spin–spin interaction with the two equivalent fluorine nuclei. The centre of the triplet is displaced by ~ 6 Hz to the side of fields of greater intensity in relation to benzene. The spin–spin splitting corresponds to ~ 24 Hz.

The ^{19}F-NMR spectrum consists of two broad bands arising from the spin–spin interaction of the fluorine nuclei with the proton. The peak of this doublet, which corresponds to a greater field strength, is located in the region 2100 Hz to the side of fields of lower intensity relative to trifluoroacetonitrile [3,6].

The mass spectra of difluoramine have also been studied in detail [4,6].

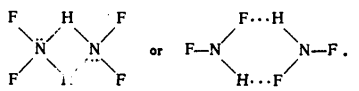
The anomalously high boiling point of difluoramine (-23.6°) compared with the value which could be expected starting from the boiling point of ammonia (-33.4°) and nitrogen trifluoride (-129°), the high dipole moment of the HNF_2 molecule, and other data given in Table 1 undoubtedly show that in the condensed phase difluoramine is a strongly associated liquid.

The difluoramine molecule is amphoteric and is capable of complex formation through hydrogen bonds with alkali metal fluorides [11–13] and Lewis basicity with several aprotic acids [14]. It is reasonable to assume that association

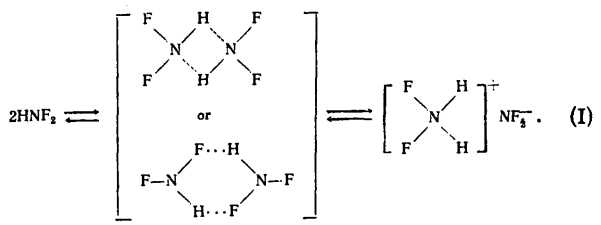
TABLE 1. Some properties of ammonia and several of its fluoro-derivatives.

Formula of compound / Characteristic	NH_3	HNF_2	$ClNF_2$	NF_3
Molecular weight	17	53	87	71
Boiling point, °C	–33	–23.6	–67	–129
Heat of vaporisation, kcal $mole^{-1}$	5581	5940	4350	2769
Trouton constant	23.3	23.7	21.0	19.94
Dipole moment, D	1.43	1.93	—	0.21
Solubility in water	very good	soluble	—	insoluble

in the liquid phase is effected by the formation of a hydrogen-bonded dimer, whose presence in solid difluoramine was shown by Craig by infrared spectroscopy [14]:



It is not ruled out that such an associate-dimer of difluoramine plays the part of an activated complex characterising the four- or six-membered transition state in equilibrium:



Difluoramine is rather readily soluble in several polar solvents, for example, in water [5,9,15,16] and, despite one assertion [2], is stable in deoxygenated aqueous and sulphuric acid solutions. Heating these solutions or non-hermetic storage leads to almost quantitative desorption of the difluoramine from them.

Preparations of 0.15 M solutions of difluoramine in 0.1 M sulphuric acid have been described [5]. On heating aqueous solutions acidified with sulphuric, nitric, phosphoric, sulphurous, or other mineral acids it can be completely expelled from them [15,17]. For example, the quantitative liberation of ~ 6.6 g HNF_2 from its solution in 100 ml 5% H_2SO_4 on heating the latter at 90° for 30 min has been described.

Difluoramine is sparingly soluble in concentrated sulphuric acid at reduced pressure and room temperature [18]. This property is utilised for its quantitative separation in preparation from triphenylmethyldifluoramine (tritylfluoramine). For example, by vacuum treatment 0.053 g HNF_2 was completely extracted from its solution in 10 ml concentrated sulphuric acid.

The solubility of difluoramine in dimethyl, ethyl methyl, diethyl, di-isopropyl, and dibutyl ethers; methylal [diethoxymethane]; dimethoxyethane; anisole; tetrahydrofuran; tetrahydropyran; and ethylene oxide has been investigated [5,19]; it forms homogeneous solutions with these solvents over a rather wide range of ratios. Solutions containing up to 10 parts by weight were obtained for dimethyl and diethyl ethers and ethylene oxide, up to 5.8 parts by weight for methylal, and 5.2 parts by weight HNF_2 for dimethoxyethane per part by weight of solvent.

The solutions of difluoramine in ethers are quite stable over a rather wide range of temperature and were patented as mono-component and two-component liquid rocket propellents [15,19]. A mixture of dimethyl ether and difluoramine, for example, is stable at from -142° to room temperature. The order of mixing of the ethers with difluoramine and also the state of aggregation of the components of the mixture (except solid) are unimportant, but the rate of mixing should be rather slow, as there is a considerable exothermic effect during mixing. All the mixtures exhibit a marked negative departure from Raoult's law, which once again confirms the hypothesis concerning the association of difluoramine in the liquid phase.

The solutions of difluoramine in dimethyl ether, diethyl ether, and ethylene oxide have been studied most thoroughly [5]. It has been found that these ethers form molecular addition compounds with difluoramine in the ratio 1 : 1, giving the composition $R_2O.HNF_2$. However, at room temperature these addition products are completely dissociated into their constituent molecules.

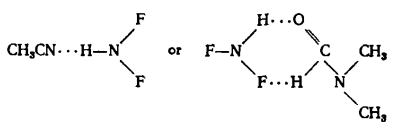
The solubility of difluoramine in methanol, ethanol, acetonitrile, dimethylformamide, and dimethyl sulphoxide has also been investigated [20]. It has been shown that equimolecular solutions of difluoramine in these solvents, like the solutions in ethers and ethylene oxide [5], behave as equilibrium systems of the form:

$$HNF_2 + X \underset{+\Delta}{\overset{-\Delta}{\rightleftharpoons}} X \cdot HNF_2$$

where X = H_2O, CH_3OH, C_2H_5OH, CH_3CN, $(CH_3)_2NCHO$, or $(CH_3)_2SO$, for which a fall in temperature favours a shift in the equilibrium to the right.

The stability of the complexes formed (adducts) depends on the nature of X. The most stable complexes are with dimethylformamide and dimethyl sulphoxide, whereas the complexes with water are distinguished by insignificant stability.

Infrared spectroscopy has shown that the complex formation in these examples is brought about by the formation of intermolecular hydrogen bonds, for example:



with the force of association falling in the sequence:

$$HNF_2 \cdot (CH_3)_2NCHO \sim HNF_2 \cdot (CH_3)_2SO > HNF_2 \cdot CH_3OH > HNF_2 \cdot H_2O$$

For some of these systems the equilibrium state is characterised as follows:

$$\ln K_{p_{HNF_2 \cdot CH_3OH}} = -\frac{4143.2}{T} + 23.22, \qquad \Delta H = 8.24 \text{ kcal mole}^{-1},$$

$$\ln K_{p_{HNF_2 \cdot CH_3CN}} = -\frac{6538.2}{T} + 31.464, \qquad \Delta H = 13.02 \text{ kcal mole}^{-1},$$

where $K_p = p^2/4$.

TABLE 2. Properties of some molecular adducts of difluoramine [5].

Ether	B.p., °C extrapolation	H_{vap}, kcal mole^{-1}	Trouton constant	Dependence of vapour pressure on temperature, $\log p_{mmHg}$ =
Dimethyl	0	7.66	28.1	$-1674/T+9.005$
Diethyl	36	7.41	24.0	$-1619/T+8.124$
Ethylene oxide	22	6.92	23.5	$-1512/T+8.015$

The examples quoted of the reversible complex formation by difluoramine with water and various organic compounds undoubtedly show that its tendency to intermolecular interaction by the formation of hydrogen bonds is one of the most important prerequisites for understanding the character of the reactivity of this compound. In this, the difluoramine molecule can evidently act either as an acceptor (through the hydrogen atom) or as a donor (through the nitrogen or fluorine atoms).

3. METHODS OF MAKING DIFLUORAMINE

Despite Ruff and Staub's claim [21,22] to have made difluoramine by the electrolysis of fused ammonium hydrogen fluoride, it is quite clear [1-3] that this compound was first obtained by Kennedy and Colburn [6] in 1959. In studying the pyrolysis of nitrogen trifluoride over arsenic in the presence of water vapour with the aim of preparing tetrafluorohydrazine, they found [6] that at 250–300° a little difluoramine is formed in addition to N_2F_4.

It is impossible to support the suggestion [6] that the appearance of HNF_2 in this process is due to the intermediate formation of arsine. The oxidative nature of the interaction of nitrogen trifluoride with arsenic and of tetrafluorohydrazine with arsine [23] obviously excludes the possibility of the formation under these conditions of such a strong reductant as arsine. Most probably difluoramine is formed as a result of the difluoramine radicals which are produced in large amounts in the defluorination of nitrogen trifluoride by arsenic:

$$NF_3 + As \xrightarrow{300^\circ} {}^\cdot NF_2 + AsF_3,$$

reacting directly with water molecules:

$${}^\cdot NF_2 + HOH \longrightarrow HNF_2 + {}^\cdot OH.$$

The great ability of the difluoramine radical to detach a hydrogen atom, a reaction which is essentially an oxidation:

$$H^\cdot + {}^\cdot NF_2 \longrightarrow [H^+ + NF_2^-] \longrightarrow HNF_2,$$

forms the basis of a group of methods for obtaining difluoramine [23]. Thus, on heating mixtures of tetrafluorohydrazine with arsine in an autoclave (1 h at 50–60°), difluoramine can be obtained in 52% yield:

$$N_2F_4 + AsH_3 \longrightarrow HNF_2.$$

The reaction of tetrafluorohydrazine with thiols also leads to the formation of difluoramine:

$$2RSH + N_2F_4 \longrightarrow 2HNF_2 + R{-}S{-}S{-}R.$$

As a result of the reaction of tetrafluorohydrazine with thiophenol at 50° in a glass reactor, difluoramine is formed in 75% yield, whereas in reaction with butanethiol in a stainless steel autoclave it is obtained in only 9% yield.

In all these instances it was very difficult preparatively to isolate the difluoramine from the gaseous reaction mass and this was done by fractional condensation of the products in a vacuum with a series of traps at -80° and below.

One variety of this group of methods is the preparation of difluoramine by heating a mixture of tetrafluorohydrazine and acetaldehyde to 150° : [24]

$$CH_3CHO + N_2F_4 \xrightarrow{150^\circ} CH_3CONF_2 + HNF_2.$$

Evidently there is an unbranched chain reaction in which $^{\cdot}NF_2$ radicals play the initiating role:

(1) $$N_2F_4 \rightleftharpoons 2{}^{\cdot}NF_2,$$

(2) $$RCHO + {}^{\cdot}NF_2 \longrightarrow R\dot{C}O + HNF_2,$$

(3) $$R\dot{C}O + N_2F_4 \longrightarrow RCONF_2 + \dot{N}F_2, \text{ etc.}$$
$$(^{\cdot}NF_2)$$

This is the more probable in that the last stage has been successfully brought about after the homolytic photolysis of biacetyl in an atmosphere of tetrafluorohydrazine[24]:

$$CH_3COCOCH_3 \xrightarrow[N_2F_4]{h\nu} 2CH_3CONF_2.$$

We think that it is not accidental that not a single instance of the formation of difluoramine in the action of tetrahydrofluorohydrazine on alcohols, carboxylic acids, or amines has yet been described, though these compounds have labile hydrogen. Furthermore, it is known[16] that the action of tetrafluorohydrazine on dimethylamine at 80° for 2 h in the gas phase leads only to the production of small amounts of methyl azide, diazomethane, and azomethane and does not give difluoramine, and the action of chlorodifluoramine on an excess of dimethylamine in ethereal solution leads to quantitative formation of tetrafluorohydrazine and dimethylammonium chloride.

On the other hand, Grzechowiak and coworkers have reported that heating certain alkanes[8] or acetone[26] with tetrafluorohydrazine leads to the removal by the $^{\cdot}NF_2$ radical of a hydrogen atom from the alkane and the formation of difluoramine and the corresponding alkyldifluoramines:

$$RH + {}^{\cdot}NF_2 \longrightarrow R^{\cdot} + HNF_2,$$
$$R^{\cdot} + N_2F_4 \longrightarrow RNF_2,$$
$$(^{\cdot}NF_2)$$

where R = CH_3COCH_2 or a hydrocarbon radical.

The authors evidently did not succeed in isolating alkyldifluoramines in the pure state, since under the conditions of the reaction they decompose into a complex mixture of resinous products.

Bumgardner[26] observed the formation of alkyl-, alkenyl-, and alkynyl-difluoramines in the photochemical reaction between tetrafluorohydrazine and certain saturated and unsaturated hydrocarbons:

$$2CH_4 + 2N_2F_4 \xrightarrow[30\ min]{h\nu} 2CH_3NF_2 + 2N_2F_2 + 2HF \quad (50\%),$$

$$CH_3CH{=}CHCH_3 \xrightarrow[h\nu]{N_2F_4} CH_3CH{=}CHCH_2NF_2 + CH_3CHFCH(NF_2)CH_3 \quad (74\%),$$

$$CH_3C{\equiv}CCH_3 + N_2F_4 \xrightarrow{h\nu} \begin{cases} CH_3C{\equiv}CCH_2NF_2 \\ CH_3CF_2C(=NF)CH_3, \\ CH_3CF{=}C(NF_2)CH_3 \end{cases}$$

Chromatographic analysis of the products of the reaction on Chromosorb impregnated with silicone oil showed the absence of difluoramine from them. The initiating role in this process on account of the loss of the hydrogen atom from the hydrocarbon was ascribed by Bumgardner solely to a fluorine atom formed in the decomposition of the excited radical $^{\cdot}NF_2$†:

$$^{\cdot}NF_2 + h\nu \longrightarrow [{}^{\cdot}NF_2^*] \longrightarrow F^{\cdot} + F\dot{N},$$
$$RH + F^{\cdot} \longrightarrow R^{\cdot} + HF.$$

† Bumgardner believed the reaction to be initiated by F· (instead of $^{\cdot}NF_2^*$) as no HNF_2 or bisdifluoramino-compounds are observed (Ed. of Translation).

However, considering the ease with which difluoramine in contact with solid materials undergoes dehydrofluorination to form fluorazene [or fluoronitrene (Ed. of Translation)], then giving difluorodiazine [dinitrogen difluoride (Ed. of Translation)][5]:

$$HNF_2 \longrightarrow HF + \dot{N}F,$$
$$2\dot{N}F \longrightarrow N_2F_2,$$

and the probability that this change can occur in the chromatographic column, then once again the chromatographic data cannot be considered completely adequate for concluding the absence of difluoramine from this process due to the removal of a hydrogen atom by the radical $^{\cdot}NF_2$.

These facts show that the formation of difluoramine can be expected in by no means all instances of the interaction of tetrafluorohydrazine with substances bearing a labile hydrogen, as has been stated[2], but only when the substance is capable of easily losing not a proton, but an atom of hydrogen, which subsequently recombines with the $^{\cdot}NF_2$ radical.

Until recently the most acceptable method for making difluoramine[4] consisted in the action of elemental fluorine diluted with nitrogen on urea at 0°. Other investigators[5,27] have often used this method. It provides difluoramine in yields which, although moderate (up to 30% on the fluorine used[5]), are evidently sufficiently stable. Taking into account that the *NN*-difluorourea being formed in this process in high yield can be almost quantitatively decomposed on heating its aqueous solutions to 90° with sulphuric acid according to the equation[15,17,27]:

$$2NH_2CONF_2 + 2H_2O + H_2SO_4 \longrightarrow 2CO_2 + 2HNF_2 + (NH_4)_2SO_4,$$

the overall practical yield of difluoramine should be considered to be considerably higher.

In a modification of this method[11] it is proposed to isolate difluoramine from the liquid which is obtained by the fluorination of urea after Lawton and Weber in a single stage by acidifying it with sulphuric acid. With this reaction a continuous process for the production of difluoramine becomes possible[15].

To obtain difluoramine by acidic hydrolytic decomposition it is possible to use the products of the fluorination of biuret, aminoguanidine, diaminourea, 5-aminotetrazole, guanidinium chloride[28], and also almost any derivative of the type:

$$RR'NCXNF_2,$$

where R and R′ can be aryl, nitroaryl, or alkyl; and X is a sulphur or oxygen atom or an NH group. These products are readily obtainable according to the equation[15]:

$$RR'NCXNH_2 + 2F_2 \longrightarrow RR'NCXNF_2 + 2HF.$$

Evidently the ability of *NN*-difluoroamido-derivatives to give difluoramine when aqueous solutions of acids act on them is one of the most important features of the reactivity of this class of compound. Mono- and di-*N*-fluorocarbamates are formed in good yield in the fluorination of alkyl carbamates with elemental fluorine in water or acetonitrile[29]:

$$H_2NCOOR \xrightarrow[H_2O \text{ or } CH_3CN]{F_2} [FHNCOOR] \xrightarrow{F_2} F_2NCOOR,$$

where R = methyl, ethyl, n-propyl, isopropyl, or n-butyl.

Like *NN*-difluorourea, the esters of *NN*-difluorocarbamic acid give difluoramine quantitatively on heating with aqueous solutions of acids:

$$F_2NCOOR \xrightarrow{H_3O^+} HNF_2 + CO_2 + ROH.$$

Difluoramine can be obtained in good yield by hydrolysis of *NN*-difluoroaminocarbonyl fluoride[30], obtained in the ultraviolet irradiation of a mixture of carbon monoxide and tetrafluorohydrazine:

(1) $$CO + N_2F_4 \xrightarrow{h\nu} F_2NCOF + COF_2 + CO_2 + NF_3,$$

(2) $$F_2NCOF + H_2O \longrightarrow HNF_2 + HF + CO_2.$$

Difluoroaminocarbonyl fluoride is hydrolysed immediately even by the action of traces of moisture; therefore on reacting with other substances in aqueous solution it behaves like difluoramine[4-6,9,11], for example:

$$2F_2NCOF + 8OH^- \longrightarrow N_2F_2 + 2CO_3^{2-} + 4F^- + 4H_2O \text{ (see Refs. 9 and 11),}$$

$$F_2NCOF + 6I^- + 5H_3O^+ \longrightarrow 2I_3^- + NH_4^+ + 3HF + 4H_2O + CO_2 \text{ (see Refs. 4 and 5).}$$

Difluoramine can be made in good yield by acid hydrolytic decomposition of *NN*-difluorosulphonyl diamide[31], which can be obtained by the fluorination of an aqueous solution of sulphonyl diamide with fluorine below -5°:

$$2F_2 + H_2NSO_2NH_2 \longrightarrow 2HF + F_2NSO_2NH_2,$$
$$F_2NSO_2NH_2 + H_2O \xrightarrow[t^\circ]{H^+} HNF_2 + HOSO_2NH_2.$$

Acidification may be effected with phosphoric or sulphuric acid of a concentration not above 1 *N*: the use of concentrated sulphuric acid is said to decrease the yield of difluoramine and increase that of tetrafluorohydrazine.

Difluoramine can be obtained just as successfully by the acid hydrolysis of some complexes of *NN*-difluorosulphonyl diamide, for example:

$$(C_6H_5)_3PO \cdot H_2NSO_2NF_2,$$

complexes which, unlike *NN*-difluorosulphonyl diamide, can be isolated pure.

The "sulphamide" method of obtaining difluoramine can be considered to be more preferable than the "carbamide", since in the final stage it does not give any gaseous products other than difluoramine, whereas in the preparation from *NN*-difluorourea it is liberated from solution as an equimolecular mixture with carbon dioxide, the separation of which presents known preparative difficulties.

The attempt to bring about the preparation of difluoramide by the vapour-phase fluorination of ammonia with elemental fluorine[32] cannot be considered successful, since this results in the formation of a complex, difficultly separable mixture of reaction products:

$$NH_3 + F_2 \longrightarrow NF_3 + N_2F_4 + HNF_2 + N_2F_2 + NH_4F.$$

A small quantity of difluoramine in a high degree of purity under laboratory conditions can be easily obtained by the decomposition of trityldifluoramine with concentrated sulphuric acid at room temperature[18]:

$$(C_6H_5)_3CNF_2 + H_2SO_4 \longrightarrow HNF_2 + (C_6H_5)_3C^+ \cdot HSO_4^- \xrightarrow{H_2O} (C_6H_5)_3COH + H_2SO_4.$$

The method ensures a 99% yield of almost pure difluoramine, which in combination with the relative accessibility of trityldifluoramine makes it extremely attractive. Trityldifluoramine in turn can be readily made from trityl chloride by reaction with tetrafluorohydrazine in the presence of mercury[18]. However, the method is of little use for technical purposes, since (as an example) 0.30 g (0.001 M) trityldifluoramine were spent in decomposition and a total of 23 cm^3 gaseous difluoramine was obtained.

The use of concentrated sulphuric acid does not prevent the quantitative formation and isolation of difluoramine and does not result in a redox reaction with the formation of tetrafluorohydrazine, as happens in the decomposition of *NN*-difluorosulphonyl amide or its complexes[31]. Probably the reason for the contradiction in these two observations lies in the different temperature conditions.

The ability of trityldifluoramine to give difluoramine with concentrated sulphuric acid is still unique among the difluoroaminoalkane series. The action of sulphuric acid on ethyl, t-isobutyl, n-butyl-, and s-butyl-*NN*-difluoramines does not lead to the formation of difluoramine[33]: these reactions are considered in detail in Section 4.

Mention must also be made of a single instance of the formation of difluoramine: ethanol acts on *NN*-difluoroacetamide to give the products ethyl acetate and difluoramine[24]:

$$CH_3CONF_2 + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HNF_2.$$

This example, like the many instances of the hydrolytic instability of the *NN*-difluoroamido-derivatives described above, suggests that they possess the properties of acid halides and that the NF_2 group has a pseudo-halogen character.

4. CHEMICAL PROPERTIES AND REACTIVITY OF DIFLUORAMINE

It is desirable to start the review of the chemical properties of difluoramine by considering its capability for complex formation with different reagents.

The amphoteric nature of the HNF_2 molecule enables difluoramine to form coordination complexes either through the acceptor properties of the hydrogen atom or through the donor ability of the nitrogen and fluorine atoms, which have sufficiently active lone electron pairs.

In investigating the interaction of a series of organic and inorganic difluoramine derivatives of the type XNF_2, including some alkyldifluoramines, difluoramine, chlorodifluoramine, and nitrogen trifluoride, with such Lewis acids as BF_3, BCl_3, PF_5, and SO_2, Craig[14] found that the reactivity of these difluoramine derivatives is determined mainly by the donor properties of the nitrogen atom, which has a lone pair of electrons.

The activity of this pair depends directly on the electronegativity of the substituents X at the nitrogen atom. The greater the electronegativity of X, the greater the deficiency of electron density which is formed at the nitrogen atom and the greater the extent to which the lone pair of electrons takes part in the compensation of this deficit, the more the electron-donor properties of the molecule appear, and their Lewis basicity falls.

Craig showed experimentally that the basic properties of the compounds of type XNF_2 fall in the sequence:

$$C_6H_5NF_2 > CH_3NF_2 \sim CD_3NF_2 > HNF_2 > ClNF_2 > N_2F_4 \sim CF_3NF_2 \sim NF_3.$$

The most stable complexes of the type $HNF_2.A$, where A is a Lewis acid, are formed by difluoramine with BF_3, BCl_3, and SO_2. When these complexes, which are quite stable at low temperatures (< -78°), are heated they either

undergo irreversible changes – for example, $HNF_2.BCl_3$, which decomposes to give chlorodifluoramine [34]:

$$BCl_3 \cdot HNF_2 \longrightarrow ClNF_2 + BF_3 + HCl + BCl_3,$$

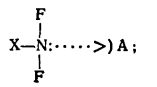
– or form equilibrium systems:

$$HNF_2.A(solid) \rightleftharpoons HNF_2(gas) + A(gas).$$

On the basis of kinetic measurements, Craig found the enthalpies of the processes and the equations which describe the temperature dependence of the pressure in the system (see Table 3).

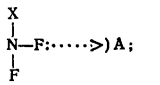
In investigating the mechanism of formation of complexes of difluoramine derivatives of the type $X-NF_2$ with Lewis acids, Craig started from the assumption of four theoretically conceivable possibilities for complex formation, due to:

(a) donor-acceptor interaction of the partners with participation of the lone pair of electrons of the nitrogen atom:

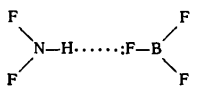


(II)

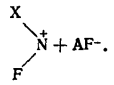
(b) donor-acceptor interaction of the partners with participation of the lone pair of electrons of the fluorine atoms, that is, by the formation of "fluorine bridges":



(c) hydrogen bonds between the hydrogen atom of the difluoramine and a nucleophilic atom of the Lewis acid:



(d) the formation of ions:

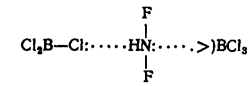


From infrared investigations Craig concluded that structure (II) best corresponds to the entire set of experimental results he obtained.

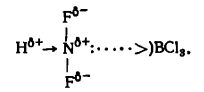
The absence from both the liquid and solid phases of difluoramine of association between the partner molecules of complex formation due to $XFN \rightarrow F \ldots A$ fluorine bridges [14] indicates greater activity by the lone pair of electrons at the nitrogen atom than by that at a fluorine atom.

Hence, although also acting as a weak base, difluoramine is capable of forming donor-acceptor bonds. The complexes thus formed are probably capable of sometimes acting as activated complexes, the formation of which can follow irreversible reactions between donor and acceptor atoms (for example, in the formation of $ClNF_2$).

According to Craig, the initial stage in the formation of chlorodifluoramine from difluoramine and boron trichloride is either the formation of a hydrogen bond:



or simple weakening of the NH bond, owing to a decrease in the electron density at the nitrogen atom:



Craig's results about the capability of difluoramine to give complexes with Lewis acids disagree with the statement of Lawton and Weber [5], who formulated their conclusions without reference to temperature interval. Craig's careful investigation showed that Lawton and Weber's conclusion about the absence of complex formation between difluoramine and Lewis acids can be correct apparently only at temperatures above 0°.

The activating role of the complex formation stage between difluoramine derivatives and Lewis acids is also shown in the dehydrofluorinations of alkyldifluoramines with BF_3, BCl_3, and PF_5. [14]

According to Craig, the first stage of the process here is the formation of complexes of the type $RNF_2.BX_3$, where R = CH_3 or C_2H_5, and X = F or Cl:

$$R'CH_2NF_2 + BX_3 \rightleftharpoons R'CH_2NF_2 \cdot BX_3, \quad \text{(III)}$$

$$R'CH_2NF_2 \cdot BX_3 \longrightarrow R'CH{=}NF + HF + BX_3,$$

$$R'CH{=}NF + BX_3 \rightleftharpoons R'CH{=}NF \cdot BX_3,$$

$$R'CH{=}NF \cdot BX_3 \longrightarrow R'C{\equiv}N + HF + BX_3. \quad \text{(IV)}$$

In citing this scheme of dehydrofluorination and unambigously considering that complex formation is brought about by the lone electron pair of the nitrogen atom, Craig contradicts some of his own observations and conclusions. The infrared spectra of the complexes of the alkyldifluoramines with Lewis acids, according to Craig's own statement, are quite complex and he did not succeed in interpreting them with sufficient certainty. In assuming that the complexes have the structure $RF_2N:BX_3$ he relied to a great extent on argument by analogy, and not on the infrared spectroscopic data.

The ease with which the complexes of the alkyldifluoramines with Lewis acids undergo irreversible decomposition with loss of hydrogen fluoride from the alkyldifluoramine molecule and the absence of a capacity for dehydrofluorination from the complexes of these Lewis acids with difluoramine enables the following propositions to be advanced.

Where difluoramine is concerned, the complexes with Lewis acids are, as Craig has shown sufficiently conclusively, formed by the lone electron pair of the nitrogen atom, but the dissociation of these complexes at elevated temperatures leads to the establishment of the reversible equilibrium considered above (with the exception of the special example of that with boron trichloride).

According to Craig's own results, the complexes of methyldifluoramine and ethyldifluoramine with boron halides and phosphorus pentafluoride are stable at temperatures below -100° and at higher temperatures "decompose irreversibly"

TABLE 3. Some characteristics of the equilibria $HNF_2.A(solid) \rightleftharpoons HNF_2(gas) + A(gas)$.

A	Expression for $\ln K_{equil}$	ΔH, kcal mole^{-1}	Note
BF_3	$-\frac{10566}{T} + 54286$	20.97	$K_p = \frac{p^2}{4}$
SO_2	$-\frac{6291.2}{T} + 35978$	12.50	

with the formation of hydrogen fluoride and the corresponding nitrile. Hence the use in Eqns. (III) and (IV) of the equilibrium sign between the left and right sides is incorrect. It is more logical to assume that in the alkyldifluoramines, when R is a hydrocarbon radical, owing to the electron donor properties of the latter the electron density at the nitrogen atom rises, as Craig observed, which naturally activates the lone electron pair at the nitrogen atom and also favours an increase in the Lewis basicity of the fluorine atom:

$$R\rightarrow\overset{\cdot\cdot}{N}F\rightarrow F:.$$

Together with steric hindrance which the alkyl radical of the Lewis acid molecule inevitably creates in its tendency to bind the lone pair of electrons of the nitrogen atom, this circumstance apparently leads to the formation of alkyldifluoramine complexes, due to fluoride bridges:

$$RCH_2\rightarrow\underset{F}{N}\rightarrow F:+)\,BF_3\longrightarrow RCH_2{-}NF{-}F:)\,BF_3,$$

and not due to the lone pair of electrons of the nitrogen atom, as occurs with difluoramine.

The decomposition of this complex when the temperature is raised leads to loss of a fluorine as a BF_4^- ion from the Lewis acid:

$$RCH_2{-}FN\,|{:}F{:}BF_3\rightarrow RCH_2{-}\overset{+}{N}F+BF_4^-.$$

The cation which is formed is stabilised by the elimination of a proton and conversion into a molecule of an *N*-fluoroimine:

$$R{-}\overset{H}{\underset{H}{C}}{-}\overset{+}{N}F\longrightarrow RCH{=}NF+H^+.$$

Subsequently, this process is repeated using hydrogen atoms at the α carbon atom, leading eventually to the formation of nitriles. The presence of hydrogen atoms at the carbon atom next to the difluoramine group is evidently proof of the condition of dehydrofluorination of the alkyldifluoramines by the Lewis acids, so that trifluoromethyldifluoramine, for example, is only very weakly associated with boron halides and no chemical reaction occurs between them [14].

The above treatment of the mechanism of dehydrofluorination is confirmed by Baum's results [33]. By studying the interaction of certain alkyldifluoramines with concentrated sulphuric acid and boron trifluoride, he showed that the process passes through the stage of formation of an *N*-fluoroiminium ion owing to the initial loss of a fluoride ion from the molecule of the difluoramine derivative:

$$R'CH_2NF_2+H_2SO_4\longrightarrow\left[RCH{=}\overset{+}{N}\begin{matrix}H\\F\end{matrix}\right]\cdot HSO_4^-+HF.$$

When R' = CH_3, Baum observed the intermediate stabilisation of the *N*-fluoroiminium ion by conversion into a molecule of an *N*-fluoroimine, which, on undergoing further dehydrofluorination by the same mechanism, was converted finally into acetonitrile:

$$\left[CH_3CH{=}\overset{+}{N}\begin{matrix}H\\F\end{matrix}\right]\xrightarrow{-H^+}CH_3CH{=}NF\xrightarrow{-HF}CH_3C{\equiv}N.$$

Baum also observed the formation of an *N*-fluoroiminium ion in other examples. When the number of carbon atoms in the radical exceeded two, a rearrangement occurred instead:

$$(CH_3)_3CNF_2+BF_3\longrightarrow\left[\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!=\!\overset{+}{N}\!<\!\begin{matrix}F\\CH_3\end{matrix}\right]\cdot BF_4^-,$$

$$C_3H_7CH_2NF_2\xrightarrow{H_2SO_4}\left[CH_2{=}\overset{+}{N}\begin{matrix}F\\C_3H_7\end{matrix}\right],$$

$$C_2H_5(CH_3)CHNF_2\xrightarrow{H_2SO_4}\left[CH_3CH{=}\overset{+}{N}\begin{matrix}F\\C_2H_5\end{matrix}\right].$$

It is also necessary to note that complex formation with Lewis acids should bring about a redistribution of the electron density in the molecule of the difluoramine derivative in the direction of its depletion at the atoms which do not participate in complex formation and increase at the atom responsible for the formation of the complex. Consequently the formation of complexes with alkyldifluoramines due to the electron lone pair of the nitrogen atom should be not facilitated, but hindered by the loss of the fluoride ion, that is, dehydrofluorination, and on the contrary, complex formation due to a fluorine bridge should promote this process, as Craig also observed.

If difluoramine could form complexes with Lewis acids through fluorine bridges, then it is probable that the ready formation of fluorazene and subsequently difluorodiazine also, would be observed, which is not so:

$$HNF_2+BF_3\longrightarrow\underset{F}{\overset{H}{>}}N\rightarrow F:)\,BF_3\longrightarrow\overset{+}{H}NF+BF_4^-,$$

$$H\rightarrow\overset{+}{N}F\longrightarrow\overset{+}{H}+\dot{N}F\longrightarrow N_2F_2$$

The complex formation by difluoramine with alkali metal fluorides, established by Lawton and coworkers [11], is well known. These investigators found that potassium, rubidium, and caesium fluorides (with an activity rising from potassium to caesium) form with difluoramine molecular complexes of 1 : 1 composition, $MF.HNF_2$ (similar to the complexes of difluoramine with the dialkyl ethers [5,19]), which decompose at even low temperatures to form the two isomers of difluorodiazine and hydrogen fluoride:

$$MF+HNF_2\longrightarrow MF\cdot HNF_2\longrightarrow MF\cdot HF+\tfrac{1}{2}N_2F_2.$$

On the basis of this reaction they have patented [35] what is perhaps the simplest and most convenient of the known methods for obtaining N_2F_2, in which the difluorodiazine is formed in almost quantitative yield and almost without impurities.

The activity of the alkali metal fluorides in this reaction rises in the sequence:

$$LiF\ll NaF<KF<RbF<CsF.$$

Careful investigation by the same authors [11] of the ability of metal fluorides to form complexes with difluoramine showed that NaF, CaF_2, and NiF_2 do not form complexes with difluoramine at -80° and below, but the complexes $KF.HNF_2$ and $RbF.HNF_2$ dissociate reversibly at elevated temperatures (from -60° to -30°). The equilibria for complexes with potassium and rubidium fluorides are characterised by the data given in Table 4.

The complex $CsF.HNF_2$ readily exploded at elevated temperatures; therefore none of the investigators has studied it in detail [11,13].

TABLE 4. Some characteristics of the equilibria[11] $MF.HNF_2(solid) \rightleftharpoons MF(solid) + HNF_2(gas)$.

MF	Expression for $\log K_{equil}$	ΔH, kcal mole^{-1}
KF	$-\frac{1467}{T}+7784$	6.7
RbF	$-\frac{2166}{T}+10338$	9.9

Dubb and coworkers have made a detailed study of the structure of the complexes $MF.HNF_2$ by infrared spectroscopy[13]. They found that potassium and rubidium fluorides form complexes with difluoramine mainly by hydrogen bonds set up between the hydrogen atom of the difluoramine molecule and the nucleophilic atom of the fluorine atom of the alkali metal fluoride (complex of type A):

$$M^+F^- \cdots \overset{\delta+}{H}—\overset{\delta-}{NF_2}.$$

Such a structure for the complexes of difluoramine with the alkali metal fluorides agrees well with the above series [11,35] for their relative tendencies to complex formation; it can also be taken as the series for the relative nucleophilicity of the fluorine atom in the fluorides, or the series for increasing electropositivity of the alkali metals.

Dubb and coworkers[13] consider that the explosive nature of the complex of caesium fluoride with difluoramine is due to the formation of the difluoramide anion NF_2^- in the complex, the existence of which they have demonstrated quite thoroughly. They think that caesium fluoride forms two types of complexes with difluoramine, one of which is identical in structure with the complexes which are formed by potassium and rubidium fluorides (type A) and the other is an ionic complex (type B): $Cs^+FH.NF_2^-$, which is responsible for the explosive nature of the adduct.

Unfortunately the authors were unable to obtain quantitative relations between the forms A and B. Possibly the explosive nature of this complex is due not only to the existence of form B, but also to the energy effect of the change of the adduct from form A to form B, that is, by the heat of the reaction:

$$\underset{\text{form A}}{Cs^+F^-\cdots\overset{\delta+}{H}—\overset{\delta-}{NF_2}} \xrightarrow{t^\circ} \underset{\text{form B}}{Cs^+\cdot HF\cdot NF_2^-} + Q.$$

For the complexes with potassium and rubidium fluorides, because of the lower electropositivities of the potassium and rubidium atoms compared with the caesium atom the nucleophilicity of the fluorine atom is insufficient for the realisation of the transformation of form A into form B.

Lawton and coworkers[11] found that the dehydrofluorination of difluoramine with formation of N_2F_2 isomers can be successfully effected also by aqueous solutions of potassium fluoride.

Thus when a 25% aqueous solution of potassium fluoride with pH 8.6 is used at room temperature, difluorodiazine can be obtained in 75% yield. The authors express the process by the equation:

$$2F^- + 2HNF_2 \longrightarrow 2HF_2^- + N_2F_2.$$

When the nucleophile is not F^- but OH^- in the form of standard buffer solutions with pH 8.0 and 9.0, difluorodiazine is formed in 25% yield.

There is a basis for supposing that this equation can be considered as the overall expression for a difluorodiazine formation process from difluoramine of at least four stages in which the nucleophilic attack:

$$B: + \overset{\delta+}{H}—\overset{\delta-}{NF_2} \longrightarrow B: \cdots HNF_2,$$

is equivalent to the formation of a type A complex in the solid phase as a result of this attack, that is, the formation of the anion NF_2^-:

$$B:\cdots H—NF_2 \longrightarrow NF_2^- + B\cdot H^+,$$

is equivalent to the transformation of a type A complex into a type B complex, with the sole difference that in the solid phase the latter is rigidly fixed, but in water it is completely dissociated into its constituent ions. Subsequent decomposition of the difluoroamide anion leads to the formation of difluorodiazine:

$$F\leftarrow\bar{N}F \longrightarrow F^- + \dot{N}F,$$

$$(\text{or } M^+ + F—\bar{N}F \longrightarrow M^+\cdots F—\bar{N}F \longrightarrow MF + \dot{N}F),$$

$$2\dot{N}F \longrightarrow N_2F_2.$$

Here M^+ is an alkali metal cation, for example potassium, etc., and B^- an anion, for example F^-, OH^-, etc.

Such a treatment is the more firmly based in that the existence of the NF_2^- anion in aqueous solutions was shown quite distinctly first by Word and Wright[36] and then by Martin[9] in their electrochemical and polarographic investigations. The latter also showed that the stability of aqueous buffer solutions of difluoramine falls with rise in temperature and pH and the decomposition products are difluorodiazine and nitrogen monoxide, the appearance of which should precede the formation of fluorazene $\dot{N}F$ due to the destruction of the anion NF_2^-:

$$NF_2^- \longrightarrow F^- + \dot{N}F.$$

Johnson[37] made analogous observations on the decomposition of aqueous solutions of *NN*-difluorourea by aqueous alkalis below 0°, when he obtained difluorodiazine, tetrafluorohydrazine, dinitrogen monoxide, etc. By using ^{15}N-labelled urea he showed that difluorodiazine is formed by an intermolecular process, the decomposition of the difluoroamide anion playing an important part:

$$NF_2^- \longrightarrow NF + F^-,$$
$$NF + NF \longrightarrow N_2F_2,$$
$$NF + NF_2^- \longrightarrow N_2F_2 + F^-,$$
$$NF + H_2NCONF_2 \longrightarrow N_2F_2 + CO_2 + NH_4^+ + F^-$$

The facts of the formation of fluorazene or fluoronitrene $\dot{N}F$ were discussed both in the investigations of the decomposition of the electron-excited radical $^*NF_2$ [26,33,38-41] and also in studying the reaction of difluoramine with primary and secondary amines [40,42,43], which we will discuss below.

The promoting action of alkali metal fluorides (potassium, rubidium) in the chlorination of difluoramine by elemental chlorine is also known[12]:

$$MF:\cdots \overset{\delta+}{H}\rightarrow\overset{\delta-}{NF_2} + Cl_2 \longrightarrow ClNF_2 + MF\cdot HCl.$$

Complexes of difluoramine with alkali metal fluorides, just like the complexes with Lewis acids, can evidently play the part of activated precursors in the reaction of the difluoramine.

These facts show that the polarisation of the nitrogen–hydrogen bond in the difluoramine molecule is sufficiently

strong for the hydrogen atom in it to be capable not only of complex formation with certain nucleophilic reagents due to hydrogen bonds, but also to be lost as a proton, so that difluoramine in aqueous solutions is a weak acid[9,36], but one which does not give salts with silver and copper nitrates even in alkaline media[5].

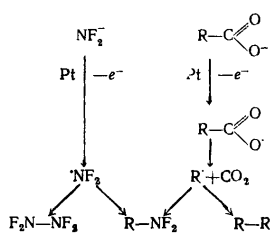
As well as complex formation, and often because of it in more complex reactions, difluoramine is capable of entering into a whole series of redox reactions.

The tendency of difluoramine (or more precisely, the difluoramide ion) to be oxidised is most clearly seen in the electrochemical preparation of tetrafluorohydrazine from it[36], when the process is localised at the stage of transfer of one electron from the anion to the platinum electrode:

$$NF_2^- \xrightarrow[\text{Pt anode}]{-e^-} \cdot NF_2.$$

Further oxidation in the electrochemical process seems impossible, thanks to the ready recombination of the difluoramine radicals to give the stable tetrafluorohydrazine molecule[36], which slowly leaves the electrolyte. This process was investigated in detail by Word and Wright[36]. It was found that the oxidation of difluoramine is possible only in acidified solutions (perchloric, sulphuric, or acetic acids) and is essentially inhibited by the presence of an oxide film on the electrode surface.

The electrochemical oxidation of difluoramine at a platinum anode can be successfully combined with the electrochemical (anodic) generation of free radicals[36]. Here, in the vicinity of the electrode, various radicals are formed in ratios which depend on the concentrations of the initial substances, and the recombination of which leads to the formation of organic difluoramine derivatives:



In the electrolysis of aqueous solutions of difluoramine in acetic, propionic, or completely deuterated acetic acids in the presence of sodium acetate, yields not below 60% of the methyl-, ethyl-, and trideuteromethyl-difluoramines were obtained in this way.

The chemical oxidation of difluoramine to tetrafluorohydrazine is easily effected by the action on aqueous solutions of HNF_2 of such oxidants as bromine, perchloryl fluoride, and oxygen[5], and also by iron(III).[9] However, the oxidation of difluoramine by an excess of oxygen-containing oxidants goes further and nitrogen oxides appear among the reaction products.

The oxidation of difluoramine to tetrafluorohydrazine with iron(III) or electrochemically seemed so effective that these processes were recommended by the authors as the best means for obtaining completely pure N_2F_4 in high yields ($\lesssim$ 70%[9,35]).

The electrochemical reduction of difluoramine at a dropping mercury electrode at various pH was first studied by Martin[9] polarographically: the reduction of difluoramine proceeds only in acid medium at potentials more negative than -1.0 V relative to the standard calomel electrode. He established that in aqueous solutions there is a single-stage, four-electron process.

Subsequently Ward and coworkers[20] showed that the electrochemical reduction of difluoramine at a dropping mercury electrode in water, methanol, ethanol, acetonitrile, dimethylformamide, and dimethyl sulphoxide goes to ammonia at potentials from -1.23 to -1.64 V relative to the standard calomel electrode, depending on the nature of the solvent and base electrolyte, for which various perchlorates were used:

$$HNF_2 + 4e^- + 2H^+ \longrightarrow NH_3 + 2F^-.$$

The authors proposed a mechanism for this process and considered the influence of solvation on the half-wave potential for the reduction of difluoramine.

The typical and most studied example of the chemical reduction of difluoramine is its reaction with acidified aqueous solutions of hydrogen iodide and potassium iodide, which goes instantly and quantitatively according to the equation[4,5]:

$$HNF_2 + 4HI = 2I_2 + NH_4F + HF,$$

and is therefore used analytically for the quantitative determination of difluoramine. Nitrogenous products of the reaction (other than ammonia) are not formed in this reaction.

The capacity of the difluoramine molecule for both oxidation and reduction evidently governs its ready disproportionation under the action of various agents, according to the equation[4,5]:

$$5HNF_2 \longrightarrow 2N_2F_4 + NH_4F + HF.$$

The process is catalysed by various solid substances, among which copper, stainless steel, urea, and lithium hydride[5] can be singled out for special activity, the reaction often going explosively.

The reaction between difluoramine and hydrogen chloride in the gas phase evidently proceeds by the same mechanism[16,44]

$$3HNF_2 + 3HCl \longrightarrow 2ClNF_2 + NH_4Cl + 2HF,$$

as does that between difluoramine and carbonyl dichloride[5]:

$$3HNF_2 + COCl_2 \longrightarrow 2ClNF_2 + \text{side products}.$$

The temperature interval 100–200° is optimal for the last reaction, but even at a high temperature tens of hours are needed for the reaction. Thus at 110° $>$ 40 h are needed to complete the reaction, and at 200° $\lesssim$ 6 h. It is emphasised[44] that the ratio of reagents must be in accordance with the above equation. The use of an excess of carbonyl dichloride favours the completion of the reaction and increases the yield of chlorodifluoramine.

The authors note[5] that despite the production of chlorodifluoramine by this means in 80% yield, the reaction is not always reproducible and is accompanied by the formation of tetrafluorohydrazine. Although the mechanism of this reaction remains unexplained, it is suggested that in the first stage hydrogen chloride is formed, which on being further contacted with difluoramine forms chlorodifluoramine by the above equation for gas-phase reaction.

The liquid-phase modification of the reaction of difluoramine with hydrogen chloride is important in practical respects[16]; it makes it easy to obtain chlorodifluoramine in yields of up to 67%. The ability of difluoramine to form complexes with water sharply reduces the explosion hazard

of the process. The reaction is carried out in aqueous solution using an alkali metal chloride and elemental chlorine, and undoubtedly proceeds by an ionic mechanism in which the decisive role belongs to the difluoramide ion on the one hand, and to chlorine or a residue of hypochlorous acid on the other:

$$NF_2^- + Cl_2 \longrightarrow ClNF_2 + Cl^-, \text{ or}$$
$$NF_2^- + OCl^- \longrightarrow ClNF_2 + O^{2-}.$$

This is the more correct in that the reaction of aqueous solutions of hypochlorous acid and sodium hypochlorite with *NN*-difluorosulphonyl diamide react quite vigorously even in the cold and this is accompanied by the formation of chlorodifluoramine in 71% yield[31]:

$$H_2N{-}SO_2{-}NF_2 + ClO^- \longrightarrow ClNF_2 + \bar{O}SO_2NH_2.$$

An analogous reaction has been described[15] in which aqueous solutions of sodium hypochlorite react with aqueous solutions of *NN*-difluorourea, when the oxidation products are chlorodifluoramine and tetrafluorohydrazine:

$$H_2N{-}CO{-}NF_2 + ClO^- \longrightarrow ClNF_2 + N_2F_4.$$

There is also an example[29] of the production of dichlorofluoramine and chlorodifluoramine by the oxidation of mono- and di-*N*-fluoroalkyl carbamates by aqueous solutions of sodium hypochlorite:

$$FHN{-}COOR \xrightarrow[H_2O]{NaClO} \left[\begin{array}{c} F \\ \diagdown \\ N{-}COOR \\ \diagup \\ Cl \end{array}\right] \xrightarrow{NaClO} Cl_2NF,$$

$$F_2N{-}COOR \xrightarrow[0-5^\circ]{NaClO} ClNF_2 + R{-}COONa.$$

Most of the known reactions of difluoramine cited above are reactions with inorganic substances. For almost all of these, reaction at high rates under conditions which favour the formation of the difluoramide anion are characteristic.

Considering difluoramine as a possible raw material for the preparation of various nitrogen fluorides it is easy to note that to obtain the desired result it is not always necessary to isolate the free difluoramine in a pure form. Either pure difluoramine or its aqueous solutions can be used for this purpose with the same success, and so also can aqueous solutions of difluoramine derivatives in which the NF_2 group has the character of an acid halide. On this basis, tetrafluorohydrazine, difluorodiazine, and chlorodifluoramine can be prepared with high yields.

There are only two examples of the interaction of difluoramine with organic compounds. Stevens and Freeman found[17] that gaseous difluoramine with solutions of alkyl or aryl nitroso-compounds in a mixture of pyridine and methylene chloride (15 : 75 ml) at 0–20° gave the corresponding alkyl- or aryl-*N'*-fluorodi-imide *N*-oxides:

$$RNO + HNF_2 \xrightarrow[0-20^\circ]{\text{pyridine} + CH_2Cl_2} R{-}\overset{\uparrow O}{N}{=}NF.$$

This reaction has been carried out on a series of nitroso--compounds, where R = phenyl; *o*-, *m*-, and *p*-tolyl; *o*- and *p*-chlorophenyl; *p*-bromophenyl; *p*-nitrophenyl; t-butyl; 2-nitro-2-propyl; 2-chloro-2-propyl; trifluoromethyl; benzyl; 2-phenylethyl; and cyclohexyl.

Simultaneously Stevens and Freeman showed that the same result can be obtained when gaseous tetrafluorohydrazine is used instead of difluoramine to react with solutions of nitroso-compounds in methylene dichloride, chlorobenzene, or carbon tetrachloride.

The last circumstance, with the known fact of tetrafluorohydrazine formation during the action of pyridine on difluoramine[5], led the authors to conclude that in both instances the formation of *N'*-fluorodi-imide *N*-oxides occurs by the very same mechanism proposed earlier by Frazer and coworkers[45] who effected a gas-phase photochemical reaction between trifluoronitrosomethane and tetrafluorohydrazine and first isolated trifluoromethyl--*N'*-fluorodi-imide *N*-oxide:

$$CF_3{-}\overset{\uparrow O}{N}{=}NF$$

Bumgardner and coworkers[42] showed that difluoramine, when condensed in a glass apparatus with an excess of an aromatic or aliphatic primary or secondary amine, deaminates the latter and gives the corresponding alkanes:

$$3RNH_2 + HNF_2 \longrightarrow 2RNH_2{\cdot}HF + N_2 + R{-}H.$$

The yield of RH reaches 77%.

With some secondary amines the reactions are:

$$\begin{array}{l} CH_2 \\ \diagup \\ NH \\ \diagdown \\ CH_2 \end{array} + HNF_2 \longrightarrow 2HF + N_2 + CH_2{=}CH_2, \qquad 80\%$$

$$\begin{array}{l} CH_2{-}CH_2 \\ | \quad\quad | \\ CH_2{-}NH \end{array} + HNF_2 \longrightarrow 2HF + N_2 + \begin{array}{l} CH_2 \\ \diagup \quad \diagdown \\ CH_2 \quad\quad CH_2 \end{array}, \qquad 40\%$$

$$(C_6H_5{-}CH_2)_2NH + HNF_2 \longrightarrow 2HF + N_2 + C_6H_5CH_2CH_2C_6H_5. \qquad 53\%$$

The authors explain the reaction with primary amines by the intermediate formation of a mono-substituted di-imide RN=NH. They consider that initially the amine promotes the α-elimination of hydrogen fluoride by the difluoramine, with formation of fluorazene:

$$RNH_2 + HNF_2 \longrightarrow RNH_2{\cdot}HF + \dot{N}F.$$

The electrophilic fluorazene in the excess of amine attacks the latter to form monosubstituted di-imide:

$$RNH_2 + \dot{N}F \longrightarrow RN{=}NH + HF,$$

which, by eliminating the nitrogen, gives an alkane, or by acting as a "trap" for the fluorazene, eliminates hydrogen fluoride and gives an alkyl azide, which was also found among the reaction products:

$$R{-}\dot{N}{=}\dot{N}{-}H + \dot{N}F$$
$$RH + N_2 \qquad RN_3 + HF.$$

With t-butylamine only ammonia and 2-methylpro-1-ene were found in the reaction products; they are formed also by the action of hydrogen chloride on this amine, which the authors take to be evidence of the acidic nature of difluoramine in relation to the amines.

Bumgardner and Freeman investigated the same reaction with certain allyl- and cyclopropylcarbinyl-amines‡ [43]. Here they observed some novelty in the reaction due rather to the unsaturated nature of the hydrocarbon radicals than to the specific effects introduced by the difluoramine. As in the previous investigation, difluoramine mainly acted as a deaminating agent.

‡ Sic. Diallyl-, allyl-, crotyl-, and 1-cyclopropylethyl-amine were studied (Ed. of Translation).

The summary of the facts given in the present review covers those reactions of difluoramine which were known up to the end of 1966. There is no doubt that the diverse reaction capabilities of difluoramine have hardly been investigated, for completely understandable reasons; in relation to different organic substances it will have many unexpected and interesting reactions, which will give a deeper understanding of the nature of this extremely interesting compound and enable the nature of the processes in which it takes part to be formulated more reliably.

5. EXPLOSIVE PROPERTIES OF DIFLUORAMINE

All the authors cited in this review without exception consider it their duty to warn readers about the extreme hazard of working with nitrogen fluorides in general and with difluoramine in particular. This danger consists in the fact that independently of the state of aggregation, difluoramine tends to spontaneous explosive decomposition for unknown reasons. Mixtures of difluoramine, like other nitrogen fluorides, with the vapours of organic substances also form explosive hazards. It is difficult to state which of the states of aggregation of difluoramine is the most dangerous but there are many indications that difluoramine itself is particularly dangerous in the solid form.

Lawton and Weber[5] note that: "... Difluoramine is extremely shock sensitive as a liquid, and even more so as a solid. The liquid is at least as detonable as nitroglycerine. The solid will detonate spontaneously when a large quantity is frozen by liquid nitrogen".

In special experiments Lawton and Weber observed over ten instances of explosion following condensation of difluoramine in quantities of 50 mg or less by liquid nitrogen, that is, at temperatures of ~ -196°. The explosions took place in the first few seconds after the trap with the difluoramine was removed from the bath of liquid nitrogen. However, they were successful more than 100 times in condensing without explosion more than 1 g difluoramine at -142° with a melting methylcyclohexane bath.

All the investigators think that at temperatures down to -142° difluoramine is comparatively harmless; they are all unanimous in the inadmissability of cooling it below this temperature and categorically forbid the use of liquefied gases (particularly liquid nitrogen) as cooling agents.

It has also been maintained[16,19] that aqueous solutions of difluoramine[16] or its solutions in ethers[19] have considerably less tendency to explode and are comparatively harmless. Nevertheless, Word and Wright[36] observed some instances of the explosion of electrolysers when the space above the aqueous electrolyte containing dissolved difluoramine communicated freely with the atmosphere. When the free space was purged with dry inert gas, they succeeded in subsequently avoiding the troubles associated with the explosion of the cells. Apparently there is also a hazard from explosions on contact of the purge gas from concentrated solutions of difluoramine with the air.

The reason for the high tendency of difluoramine to spontaneous explosive decomposition probably lies in the wholly amphoteric nature of its molecule and the dual nature of its reactivity to redox interaction. This opens a path to intermolecular disproportionation, which is also accompanied by such highly exothermic processes as the formation of hydrogen fluoride, elemental nitrogen, and nitrogen trifluoride. The activation of this process is apparently very small and can be greatly reduced by the catalytic action of various solid substances. The initial impulse can be produced either inside the system by effective catalysis, or externally by an action of accidental origin. Subsequent processes probably develop autothermically and possibly also autocatalytically.

Instances of the remarkable explosive decomposition of difluoramine after cooling below -196° should be placed in a special category. Undoubtedly such behaviour of difluoramine is connected with some energetic effects which take place inside or on the surface of the crystals of solid difluoramine. It is not ruled out that the reason for this phenomenon lies in the ionic structure of the crystal lattice of solid HNF_2, although Craig[14] also did not succeed in observing any essential difference in the infrared spectra of gaseous and solid difluoramine at -196°.

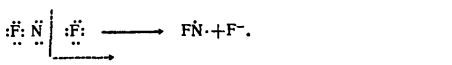
Here infrared spectroscopy cannot give the necessary information for a categorical decision as to the absence of ionisation from solid difluoramine. Just the fact of the similarity of the absorption frequencies for gaseous and solid difluoramine in the infrared region cannot serve as sufficient proof of the absence of a change of difluoramine into an ionic state at ~ -196°. One of the explanations of this important phenomenon can be a useful subsequent approach, which follows logically from the discussion in Section 2 of the present review.

In the liquid state equilibrium (I) is apparently almost wholly displaced to the left, that is, to the side of the molecular form of the dimer. The rigid fixation of the ions NF_2^- and $[H_2NF_2]^+$ at the nodes of the crystal lattice which is a consequence of deep cooling rules out the possibility of a change of the ionic form of the dimer into the molecular form and greatly facilitates the displacement of equilibrium (I) to the right. This change, under a suitable regime of cooling and crystallisation (which is evidently realised at -196° and below, but more correctly in attaining these temperatures) ends the almost complete fixation of the difluoramine as an ionic dimer. On raising the temperature the change of the difluoramine into the liquid state should be accompanied by intensive association of the ions into the molecular form of the dimer with a perceptible thermal effect.

The energy liberated is evidently sufficient to surmount the low activation barrier and start the process of rapid autothermal (possibly, also autocatalytic) decomposition of difluoramine, which is explosive in nature.

The many statements of various authors on the instability of the difluoroamide anion and the ease with which it decomposes into fluoronitrene and the fluoride anion have been given above. In all the instances of such decomposition conditions were created for suppressing the dissociation of difluoramine with formation of the NF_2^- ion (increase in the pH of the aqueous difluoramine solutions above 7, heating them, the action of ionising complex-forming agents, such as potassium fluoride, rubidium fluoride, and especially caesium fluoride, etc.). Therefore there are grounds for assuming that explosion in the processes in which difluoramine participates (because of the explosive decomposition of the latter) should be expected in those instances when conditions are created for the formation of high concentrations of difluoramido-anions in the absence of conditions for their recombination into stable molecules of the $X-NF_2$ type, in which the X–N bond will have a more covalent character than the H–N bond in difluoramine.

The NF_2^- ion is a species limitingly saturated with electrons, which should stimulate its tendency to stabilisation, leading to a decrease in this saturation, by the elimination of a fluoride anion:



Depending upon the conditions (the presence or absence of solvents and catalysts) the temperature, the difluoramine concentration, pH of the medium or basicity of the reagent, etc.) the process can proceed either quietly (for example, in aqueous alkaline solutions or under the action of potassium and rubidium fluorides) or explosively (for example, in pure difluoramine or upon reaction with caesium fluoride).

It cannot be excluded that the existence of the difluoramide anion for a sufficiently prolonged period outside the molecule of difluoramine, adducts, transition states, etc. (that is, not in a bound state) is impossible in general.

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ACIDITY FUNCTIONS OF AQUEOUS SOLUTIONS OF STRONG ACIDS

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1. ACIDITY SCALE FOR AQUEOUS SOLUTIONS OF STRONG ACIDS

In investigating the kinetics of chemical processes in a homogeneous solution it is necessary to take into account the influence of the solvent on the thermodynamic properties of the reactants. The properties of the medium are of particular importance in chemical reactions taking place in aqueous solutions of strong acids and bases. The great tendency to form hydrogen bonds and the higher concentration of ions in such solutions promotes the formation of various complexes and ions with participation of the reagents.

In kinetic equations for liquid-phase processes allowance is made for the effect of the medium on the thermodynamic properties of the reagents, intermediates, and activated complex by the use of activity coefficients. In solutions of acids and bases, the reagents are usually ionised. In most instances the ionised form exhibits a greater reactivity than the un-ionised form. The catalytic action of an acid or base in such instances consists in the conversion of the reagent into an ionised form. The possibility of the chemical process occurring at the moment of collision of the reagent with a proton, hydroxide ion, or molecules of undissociated acids and bases is also not ruled out. The kinetic equation for a chemical reaction will be the same for processes in which the species capable of reaction are ions formed in the interaction of the reagent with an acid or base (if the relative concentration of the ions is small) and for processes in which the rate-limiting state occurs during the collisions of the reagent molecules with protons or hydroxide ions.

We will consider the chemical reaction for the conversion of substance M into Q taking place in an acid medium. The process is first order with respect to M. It is assumed that the ionised form MH^+ is reactive. The MH^+ concentration is low in comparison with that of M. The rate of reaction W is expressed by Eqn. (1):

$$W = \frac{dC_Q}{dt} = k\frac{a^*}{f^*} = k'\frac{a_M a_{H^+}}{f^*} = k'\frac{C_M a_{H^+} f_M}{f^*}. \qquad (1)$$

$$\frac{W}{C_M} = k_{eff} = k' a_{H^+}\frac{f_M}{f^*},$$

where a^*, a_M, and a_{H^+} are the activities of the activated complex, the reacting substance M, and the proton respectively; C_M is the concentration of M; f^* and f_M are the activity coefficients of the activated complex and substance M.

According to Eqn. (1) the change in k_{eff} is connected with change in the quantity $a_{H^+}(f_M/f_{MH^+})$. In aqueous solutions of strong acids the protons are present as hydroxonium ions; therefore the activity of protons a_{H^+} must be expressed in terms of the concentration of hydroxonium ions $C_{H_3O^+}$ and the activity coefficient of the protons f_{H^+}:

$$a_{H^+}\frac{f_M}{f^*} = C_{H_3O^+} f_M \frac{f_{H^+}}{f^*}.$$

The experimentally observed proportionality between k_{eff} and the concentration of hydroxonium ions $C_{H_3O^+}$ in extremely dilute solutions of acids is connected with the constancy of the ratio $f_M f_{H^+}/f^*$.

In concentrated aqueous solutions of strong acids k_{eff} rises more sharply than the hydroxonium ion concentration; this is connected with an increase in the ratio $f_M f_{H^+}/f^*$. Consequently, to predict how the catalytic activity of an acid medium varies with change in the acid concentration it is necessary to know how the quantity $a_{H^+}(f_M/f^*)$ varies. The activity coefficient of the un-ionised form f_M can be measured. The activity coefficients f_{H^+} and f^* cannot be measured experimentally in isolation. Here assumptions must be made which allow measurable quantities to be introduced into the kinetic equation. When an activated complex is formed from a molecule of the reagent and a proton, then in composition and charge it corresponds to the ionised form of the reagent. Therefore it can be taken that as the composition of the medium is varied the activity coefficients of the activated species f^* and of the protonised form f_{MH^+} will change similarly. On making this assumption, f^* in Eqn. (1) can be replaced by f_{MH^+}.

$$k_{eff} = k' a_{H^+}\frac{f_M}{f_{MH^+}}.$$

The change in the catalytic activity of the acid medium is determined by the activity of the protons a_{H^+} and by the ratio of the activity coefficients of the un-ionised and ionised forms of the reagent. The proton activity a_{H^+} is determined by the properties of the medium. The activity coefficients f_M and f_{MH^+} reflect the properties of the reagent M dissolved in the acid. The quantity $a_{H^+}(f_M/f_{MH^+})$ also characterises the ratio of the concentrations of the protonated and unprotonated forms of the substance dissolved in the acid.

We will use k_{BH^+} to denote the equilibrium constant for the ionisation of substance B, expressed in terms of activity:

$$B + H^+ \rightleftharpoons BH^+,$$

$$k_{BH^+} = \frac{a_B a_{H^+}}{a_{BH^+}} = \frac{C_B a_{H^+} f_B}{C_{BH^+} f_{BH^+}}.$$

Hammett has proposed[1] that in concentrated aqueous solutions of strong acids the change in the ratio f_B/f_{BH^+} is determined by the properties of the acid medium and is independent of the chemical nature of the substance. Hence according to Hammett the following equality holds for solutions of substances (for example, M, B, C, and D):

$$\frac{f_M}{f_{MH^+}} = \frac{f_B}{f_{BH^+}} = \frac{f_C}{f_{CH^+}} = \frac{f_D}{f_{DH^+}}.$$

If Hammett's hypothesis is correct, then it becomes possible to find a quantitative characteristic for the ionising ability of acid media. Kinetic and indicator methods can be used for this purpose.

To obtain a quantitative measure of the catalytic activity of the acid medium by the kinetic method it is necessary to study the kinetics of some process over the required concentration range of the solution of the acid. A simple unimolecular chemical reaction for which the ionisation mechanism and rate-determining steps have been established in detail should be chosen for this purpose. It is desirable that the degree of ionisation of the reagent should be negligible over the whole concentration range of the acid, that is, the reagent should be almost wholly in its un-ionised form. When on going from dilute to concentrated solutions of a strong acid the mechanism of the process and also the activation energy and preexponential factor of the rate-determining step remain unchanged, the rate constant of such a process could serve as a quantitative measure of the catalytic activity of the acid media. The problem is to select a chemical process for which the rate constant at constant temperature would change by 12–14 orders of magnitude on changing the acid concentration.

Modern techniques of kinetic investigation allow processes to be studied where the rate constant varies only by 4–5 orders of magnitude at constant temperature. It is therefore necessary to choose several reagents with different reactivities. However, there is then no certainty that the reagents chosen as the models ionise by the same mechanism and that in all instances the mechanism of the rate-limiting step is the same.

A quantitative measure of the ionising ability of aqueous solutions of strong acids over a wide range of concentrations can be obtained using the indicator method proposed by Hantzsch[2] and worked out in detail by Hammett. By indicator is meant a chemical substance which is ionised in solutions of acids and bases, the un-ionised and ionised forms of which have different absorption spectra. An indicator should be chemically stable in the medium being investigated.

The concentrations of the ionised and un-ionised forms of the indicators are determined spectrometrically.

The simplest type of ionisation is protonation. This is an acid–base process, as a result of which base B is converted into acid BH^+, Eqn. (2). With a rather large number of substances ionisation finishes at the protonation stage.

In the ionisation of alcohols and organic acids, the ionised form can be dehydrated:

$$\left.\begin{aligned} &BOH + HA \rightleftharpoons BOH_2^+ + A^- \\ &BOH_2^+ \rightleftharpoons B^+ + H_2O \end{aligned}\right\} \qquad (3)$$

The protonated form BH^+ and also the cations B^+ which are formed in the dehydration of the ions BOH_2^+ can form ion pairs:

$$\left.\begin{aligned} &BH^+ + A^- \rightleftharpoons BH^+.A^- \\ &B^+ + A^- \rightleftharpoons B^+A^- \end{aligned}\right\} \qquad (4)$$

The possibility of the reagent forming a specific complex with some acid or with the solvent cannot be excluded. The ionisation mechanism is determined by the chemical structure of the reagent and by the properties of the medium.

Naturally, in studying the ionising ability of a medium by some mechanism indicators must be chosen which ionise by the same mechanism. To establish an acidity scale, Hammett selected a series of indicators which are mainly derivatives of the nitroanilines. The ionisation of these indicators proceeds by Eqn. (2). Such indicators are termed simple. Hammett took the equilibrium constant of process (2), K_{BH^+} as a measure of the strength of the base. The negative logarithm of the quantity K_{BH^+} is denoted by pK_{BH^+}:

$$pK_{BH^+} = -\log K_{BH^+}.$$

K_{BH^+} for strong bases is small and pK_{BH^+} is positive. The weaker are the basic properties of the substance, the greater the value of K_{BH^+} and the more negative the value of pK_{BH^+}.

Hammett proposed that the quantity $a_{H^+}(f_B/f_{BH^+})$ be termed the acidity of the medium. This is denoted by the symbol h_0 and its negative logarithm is termed the acidity function and given the symbol H_0:

$$h_0 = a_{H^+}\frac{f_B}{f_{BH^+}}; \qquad H_0 = -\log h_0.$$

On taking logarithms of Eqn. (2) for the constant K_{BH^+} and replacing $-\log K_{BH^+}$ by pK_{BH^+} and $-\log a_{H^+}(f_B/f_{BH^+})$ by H_0, we obtain an equation which relates the acidity function of the medium to the ratio of the concentrations of the ionised and un-ionised forms of the indicators:

$$H_0 = pK_{BH^+} + \log\frac{C_B}{C_{BH^+}}. \qquad (5)$$

If the acidity of the medium is known it is possible to calculate the basicity constant and the ratio of the concentrations of the base and the conjugate acid form of the substance. Hence to measure the acidity function of the medium by the use of some indicator it is necessary to know its basicity constant (K_{BH^+}) and the ratio of the concentrations of the un-ionised and ionised forms (C_B/C_{BH^+}) in the given medium. The concentrations C_B and C_{BH^+} are usually measured spectrophotometrically or colorimetrically. A single indicator can be used to investigate a medium whose acidity function changes within the limits of 2–3 units, which corresponds to a change in the C_B/C_{BH^+} ratio from 30–10 to 0.1–0.03. To investigate a medium with a wider range of acidities, several indicators must be used.

Infinite dilution of an aqueous solution of a strong acid is selected as the standard state for the scale. In an infinitely dilute aqueous solution the activity coefficients f_B and f_{BH^+} are taken to be unity and the thermodynamic activity of the protons is taken as numerically equal to the hydroxonium ion concentration. In such solutions the acidity of the medium equals the hydrogen ion concentration, and H_0 equals the pH.

The essence of the indicator method of measuring H_0 consists in determining pK_{BH^+} and the values of C_B/C_{BH^+} of the indicators in the medium of unknown acidity. At first it is necessary to find the values of pK_{BH^+} for the indicators, which are strong bases, for which the quantity C_B/C_{BH^+} can be determined in extremely dilute solutions of acids, where $h_0 = C_{H_3O^+}$. For example, aminoazobenzene (which we will denote by the symbol B) is already appreciably ionised in 10^{-4} m HCl† and almost completely so in 0.024 m HCl. From the dependence of $\log(C_B/C_{BH^+})$ for aminoazobenzene on the concentration of the acid in the range of C_{HCl}, its pK_{BH^+} is calculated by Eqn. (5). Another indicator is chosen for the determination of the acidity of more concentrated solutions of hydrochloric acid, for example, benzeneazodiphenylamine, which is a weaker base than aminoazobenzene. This indicator (which we will denote by the symbol C) is only partly ionised in 1×10^{-4}–2×10^{-2} m HCl and is completely ionised in more concentrated solutions, where $-\log C_{H_3O^+}$ is no longer equal to the pH.

We will compare the logarithms of the ratios of the concentrations of the un-ionised and ionised forms for the two indicators mentioned above (for example, B and C) in the same solution of acid:

$$-\log a_{H^+} = pK_{BH^+} + \log\frac{C_B}{C_{BH^+}} + \log\frac{f_B}{f_{BH^+}} = pK_{CH^+} + \log\frac{C_C}{C_{CH^+}} + \log\frac{f_C}{f_{CH^+}},$$

or

$$pK_{BH^+} - pK_{CH^+} = \log\frac{C_C}{C_{CH^+}} - \log\frac{C_B}{C_{CH^+}} + \log\frac{f_C f_{BH^+}}{f_{CH^+} f_B}.$$

† Here and subsequently the symbol m denotes the molality of the solution [in the translation, *m* is employed as the symbol for the molality and m as the abbreviation for the unit of molality, as usual (Ed. of Translation)].

When

$$\frac{f_C f_{BH^+}}{f_{CH^+} f_B} = 0,$$

it becomes possible to determine pK_{CH^+} of the indicator C, provided pK_{BH^+} of another indicator B and the quantities C_B/C_{BH^+} and C_C/C_{CH^+} in the same medium are known.

$$pK_{BH^+} - pK_{CH^+} = \log \frac{C_C}{C_{CH^+}} - \log \frac{C_B}{C_{BH^+}}. \quad (6)$$

Since pK_{BH^+} of aminoazobenzene is determined in extremely dilute solutions‡, where $H_0 = pH = -\log m_{H_3O}$, then Eqn. (6) can be used to calculate pK_{CH^+} of the less basic indicator, for example, benzeneazodiphenylamine. By determining pK_{CH^+} by Eqn. (5), the acidity of solutions of stronger acids can be calculated where the ratio of the concentrations of the un-ionised and ionised forms of benzeneazodiphenylamine can be measured with good accuracy. To measure H_0 of more concentrated solutions, an indicator D is chosen which exhibits an even lower basicity but partly overlaps the region of acid concentrations where the indicator C is still incompletely ionised. pK_{DH^+} of the indicator and H_0 for the acid solutions are calculated as described above.

Hence by means of several indicators the acidity function is measured over a wide range of concentrations of aqueous solutions of strong acids. For example, to measure the acidity function of the $HCl-H_2O$ system from dilute solutions to 16 M HCl, it is necessary to use seven or eight indicators, and to measure H_0 of the $H_2SO_4-H_2O$ system from dilute solutions to 100% H_2SO_4 10–12 indicators are required.

2. INDICATORS FOR MEASURING ACIDITY FUNCTIONS

Table 1 gives the indicators used for measuring acidity functions and the values of their pK_{BH^+}. The ionisation of such indicators involves the addition of a proton. In acid media the indicator is present in two equilibrium forms: un-ionised and ionised.

Cryoscopic and electrical conductivity results are usually used to establish the ionisation mechanism. 100% sulphuric acid acts as an ionising solvent. The indicators chosen by Hammett for measuring H_0 were investigated cryoscopically by Hammett and coworkers[6] and also by other authors[7]; the latter[7] also investigated the electrical conductivity of the solutions. The value of the van't Hoff i factor for simple indicators is near or equal to 2. On this basis it is concluded that when these substances ionise two species are formed:

$$B + H_2SO_4 \rightleftharpoons BH^+ + HSO_4^-. \quad (7)$$

This conclusion does not seem unambigous. The i factor being 2 only signifies that in 100% sulphuric acid and in H_2SO_4 solutions with low water and sulphur trioxide concentrations (sulphuric acid only slightly diluted with water and with a low oleum concentration) the substance ionises according to Eqn. (7). On the basis of this fact it is impossible to maintain that the indicator is present solely as an ionised and an un-ionised form also in more dilute aqueous solutions of sulphuric acid, when the concentration of HSO_4^- anions is high. In 100% sulphuric acid§ the HSO_4^- ions are formed as a result of autoprotolysis:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-,$$

and their concentration is not high. For example, at 25° the concentration of HSO_4^- anions in 100% H_2SO_4 is $\sim 3 \times \times 10^{-2}$ M.[8,9] In 78–80% H_2SO_4 the concentration of HSO_4^- anions is 10.6 M at 25°.[10,11]

The possibility of the ion pairs $BH^+.HSO_4^-$ being formed in solutions of acids where there is a high concentration of anions is not ruled out:

$$BH^+ + HSO_4^- \rightleftharpoons BH^+.HSO_4^-.$$

In this instance the dissolved indicator or reagent will now be present in the acid solution as the equilibrium forms: un-ionised form, protonised form, and ion pair. When the indicators form ion pairs over some range of acid concentrations then they can be used for measurements of H_0 only if it is possible to determine the concentrations of all

TABLE 1*.

Values of pK_{BH^+} of acid indicators (at 22–26°)

Indicator	pK_{BH^+} in $HCl-H_2O$	pK_{BH^+} in $HBr-H_2O$	pK_{BH^+} in $HClO_4-H_2O$	pK_{BH^+} in $H_2SO_4-H_2O$	pK_{BH^+} in HNO_3-H_2O	pK_{BH^+} in $P_2O_5-H_2O$
p-Aminoazobenzene	+2.82	—	+2.82	—	—	—
m-Nitroaniline	+2.50	—	+2.50	—	—	—
2,4-Dichloroaniline	+2.0	—	—	—	—	—
Benzeneazodiphenylamine	+1.42	—	—	—	—	—
p-Nitroaniline	+1.0	+0.9	—	+1.0	+1.03	+1.0
Diphenylamine	+0.78	—	—	+0.77	—	—
o-Nitroaniline	−0.29	−0.23	−0.29	−0.33	−0.28	−0.2
Pyrocatecholsulphonic acid	−0.08	—	—	—	—	—
NN-Dimethyl-2,4-dinitroaniline	—	—	—	−1.0	—	—
4-Chloro-2-nitroaniline	−0.99	—	−1.07	−1.02	−1.11	−0.98
5-Chloro-2-nitroaniline	−1.44	−1.45	—	−1.55	—	−1.6
2,5-Dichloro-4-nitroaniline	—	—	−1.79	−1.90	—	—
2-Chloro-6-nitroaniline	—	—	−2.41	−2.43	—	—
4-Nitrodiphenylamine	−2.37	—	—	−2.50	—	−2.28
2,6-Dichloro-4-nitroaniline	—	—	−3.2	—	−2.55	—
2,4-Dichloro-6-nitroaniline	−3.33	−3.24	—	−3.28	−3.3	−3.02
2,4-Dinitroaniline	−4.58	−4.39	−4.26	−4.45	—	−4.96
2,6-Dinitroaniline	—	—	−5.25	−5.64	—	—
4-Chloro-2,6-dinitroaniline	—	—	−6.12	−6.25	—	—
2,4-Dinitro-1-naphthylamine	—	—	−6.5	—	—	—
6-Bromo-2,4-dinitroaniline	—	—	−6.69	−7.09	—	—
3-Methyl-2,4,6-trinitroaniline	—	—	−8.56	−8.34	—	—
3-Bromo-2,4,6-trinitroaniline	—	—	−9.77	—	—	—
2,4,6-Trinitroaniline	—	—	—	−9.98	—	—
p-Nitrotoluene	—	—	—	−11.27	—	—
p-Chloronitrobenzene	—	—	—	−12.63	—	—
Nitrobenzene	—	—	—	−12.19	—	—
2,4-Dinitrotoluene	—	—	—	−13.53	—	—
m-Nitroanilinium cation (second protonisation of *m*-nitroaniline)	—	—	—	−14.14	—	—

pK_{BH^+} at other temperatures

Indicator	Temperature, °C		
	40	60	80
p-Nitroaniline	+0.81	+0.60	+0.43
o-Nitroaniline	−0.41	−0.55	−0.70
4-Chloro-2-aniline	−1.17	−1.28	−1.41
2,4-Dichloro-6-nitroaniline	−3.07	−3.14	

* The errors in the determination of the pK_{BH^+} of the indicators are not given in Table 1, as this problem receives detailed discussion in Section 4. Pyrocatecholsulphonic acid is used as an indicator for determining the acidity of aqueous solutions of hydrochloric acid in the presence of ions of copper(I) chloride[4] at 20–80°. New information has been published recently[5] on the values of pK_{BH^+} for *p*-nitroaniline at elevated temperatures: at 30°, 40°, 50°, and 60°, it is 0.96, 0.9, 0.83, and 0.77 respectively.

‡ Before Paul's work[3], pK_{BH^+} for strong bases were determined by comparison of $\log (C_B/C_{BH^+})$ with the logarithm of the mean ionic activity $a_\pm$. When f_B is constant in very dilute solutions of acids the activity coefficient of the ionised form f_{BH^+} changes according to the Debye–Hückel law. Therefore it is correct to compare $\log (C_B/C_{BH^+})$ with the H_3O^+ ion concentration. Then the electrostatic contributions to f_{H^+} and f_{BH^+} are reduced.

§ Here and subsequently weight percentages of acids are given.

three forms separately. However, this is a rather difficult task. The spectrophotometric method in such instances is inapplicable since the free ions and ion pairs have similar absorption spectra.

It can be reliably stated that during the ionisation of indicators chosen for the measurement of acidity function free ions are formed in dilute solutions of strong acids and close to 100% H_2SO_4, where the concentration of anions is low. As for the region of moderate acid concentrations, where the anion concentration is high, there is still no direct proof of the absence of the ion pairs $BH^+.HSO_4^-$ from such solutions, but there are certain facts which can serve as indirect evidence that the measurable ratio C_B/C_{BH^+} for the indicators characterises the acidity of the medium h_0. The unimolecular reaction selected must be one which can be investigated in both concentrated and dilute solutions of the acid, for example, sulphuric acid, which encompass 7–8 units of the H_0 scale (from +1 to -7 units). The degree of the ionisation of the reagent should be negligible ($C_{BH^+} \ll C_B$) over the whole H_0 range being investigated. When k_{eff}/h_0 = const for all the solutions, this will be proof that in both concentrated and dilute solutions of the acid the mechanism of ionisation is the same.

As already mentioned, it is difficult to select a unimolecular chemical reaction for which the dependence of k_{eff} on H_0 can be studied over such a wide H_0 range under the condition $C_{BH^+} \ll C_B$. Nevertheless a single example can be given: the hydrolysis of β-propiolactone in sulphuric acid. This hydrolysis¶ has been studied in aqueous solutions of sulphuric acid from dilute solutions to 65% H_2SO_4. At 25°, k_{eff} increases in proportion to the acidity of the medium [13]. It is interesting to investigate a similar reaction over a wider range of acid concentrations. For this purpose it would be possible to select the exchange of hydrogen for deuterium and the subjects of the investigation could be the very indicators which are used to measure H_0. There are also considerations based on the method of measurement of the quantity C_B/C_{BH^+}. The un-ionised forms of nitroaniline indicators absorb, and the ionised forms do not absorb, in the visible region of the spectrum. The concentration of the un-ionised form C_B is determined from the intensity of the colour of the indicator solution in the visible region of the spectrum. The concentration of the ionised form C_{BH^+} is determined as the difference between the total concentration of the indicator and C_B.

The formation of ion pairs cannot be deduced from the measurements of the C_B/C_{BH^+} ratio when salt formation starts under conditions where the indicator is present almost entirely as the ionised form. When the salt-formation constant is such that ion pairs are formed in solutions with a low degree of protonation, it is impossible to determine C_B/C_{BH^+} from the change in the colour of the solution.

The problem of possible ion pair formation in the ionisation of acid–base indicators in concentrated acids requires detailed investigation. It is especially important to show the possibility of ion-pair formation in sulphuric acid solutions containing from 65 to 90% H_2SO_4 and in aqueous solutions of nitric acid with >60% HNO_3. Not all the substances which are used to measure H_0 satisfy the requirements applicable to indicators.

In concentrated solutions of sulphuric acid benzalacetophenone is unstable and undergoes isomerisation [14]. It is also unstable in polyphosphoric acid solutions [15]. Anthraquinone has several absorption bands in the visible and ultraviolet regions of the spectrum. On changing the acid concentration, in addition to the change in its degree of ionisation there is a displacement of the absorption maximum. Owing to the shift in the absorption maxima of *p*-nitrodiphenylamine and anthraquinone it is impossible to determine their degree of ionisation accurately.

Benzalacetophenone, anthraquinone, and *p*-nitrodiphenylamine are unsuitable for measuring the acidity of the medium. With *N*-substituted nitroanilines the concentration of the un-ionised form in aqueous solutions of sulphuric [16] and nitric [17] acids — and also in solutions of sulphuric acid in acetic acid [18] — falls anomalously. It can be assumed that in these materials ion pairs are formed during ionisation as well as the protonated species†.

As already mentioned above, a spectrophotometric method is now used for determining the concentrations of the ionised and un-ionised forms of indicators. The degree of ionisation of the indicator is most frequently determined by measuring the absorption coefficient at a single wavelength which is convenient for measurements. With the indicators of the nitroaniline series the absorption intensity is measured at some wavelength in the visible region of the spectrum. When the change in the spectrum of an indicator on raising the acid concentration is due not just to the appearance of an ionised form but also to a change in the optical properties of the medium, then it is difficult to judge the degree of ionisation of the indicator from the optical density of the solution. Usually in measurements of H_0 of acids the applicability of Beer's law is verified for particular wavelengths and during this the indicator concentration is varied over wide limits in solutions with the same acid concentration. The absorption coefficient for some form (ionised or un-ionised) is determined in solutions of acid with such an acidity that one of the forms is almost absent. In calculating C_B and C_{BH^+} it is assumed that the absorption coefficient of the forms B and BH^+ does does not depend on the composition of the medium in the range of acid concentrations at which the measurements are made. To avoid any possible effect when the medium is changed, the absorption coefficient of the un-ionised form is determined in acid solutions in which the ratio $C_B/C_{BH^+} \simeq 100$, and the absorption coefficient of the ionised form in solutions with $C_B/C_{BH^+} \simeq 0.01$. There are occasions when the change in the degree of ionisation of the indicator is not the only reason for a change in the spectrum. An example of this is the spectrum of 6-bromo-2,4-nitroaniline in sulphuric acid solutions [19]. This indicator has maximum absorption at 360 nm, due to the un-ionised form. In solutions of sulphuric acid with <67% H_2SO_4, the indicator is almost completely in the un-ionised form. In more concentrated solutions of the acid the intensity of the absorption maximum decreases (Fig. 1). The absorption coefficient also decreases at longer wavelengths. The position of the absorption maximum is almost unchanged in the interval 59–98% H_2SO_4, where ionisation of this substance takes place. When the absorption coefficients of the ionised and

¶ The hydrolysis of β-propiolactone has a complex mechanism. As Long and coworkers have shown [12], the experimentally observable rate constant is the sum of the rate constants of a non-catalytic and a catalytic process. Here we are considering the dependence of the rate constant of the catalytic process of hydrolysis on the acidity of the medium. This process is unimolecular.

† Possibly, in the ionisation of *N*-substituted nitroanilines, Hammett's hypothesis of the equality of the ratios of the activity coefficients of the un-ionised and ionised forms is not satisfied.

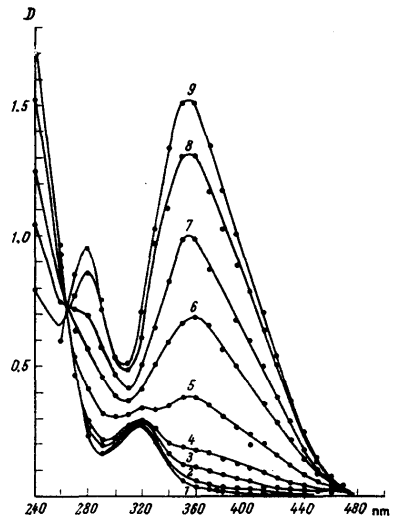

Fig. 1. Absorption spectra of 6-bromo-2,4-dinitroaniline in aqueous solutions of sulphuric acid with concentrations from 58.86 to 98.21%, from Vinnik and coworkers[19]. The optical densities D were obtained for the same indicator concentration. H_2SO_4 concentrations, %: 1) 98.21; 2) 88.07; 3) 85.24; 4) 82.72; 5) 79.93; 6) 77.5; 7) 75.36; 8) 72.18; 9) 58.96.

TABLE 2. Values of $\log(C_B/C_{BH^+})$ for 6-bromo-2,4-dinitroaniline, calculated from intensities at different wavelengths and from the area of the absorption contour from λ_{max} to the side of greater wavelengths.

H_2SO_4, %	Wavelength, nm	$\log\frac{C_B}{C_{BH^+}}$	H_2SO_4, %	Wavelength, nm	$\log\frac{C_B}{C_{BH^+}}$	H_2SO_4, %	Wavelength, nm	$\log\frac{C_B}{C_{BH^+}}$
85.24	280	−1.32	79.93	280	−0.46	75.36	280	+0.26
	360	−1.19		360	−0.50		360	+0.24
	370	—		370	−0.49		370	+0.24
	380	−1.15		380	−0.49		380	—
	390	−1.13		390	−0.44		390	+0.29
	400	−1.11		400	−0.41		400	+0.37
	410	—		410	−0.40		410	+0.38
	420	−1.18		420	−0.36		420	+0.41
	430	−1.02		430	−0.31		430	+0.54
	440	—		440	−0.27		440	+0.55
	450	—		450	−0.16		450	+0.53
	from area	−1.21		from area	−0.52		from area	+0.30
82.72	280	−1.03	77.51	280	−0.06			
	360	−0.96		360	−0.1			
	370	−0.90		370	−0.05			
	380	−0.90		380	−0.04			
	390	−0.87		390	−0.02			
	400	−0.83		400	−0.01			
	410	−0.82		410	+0.01			
	420	−0.80		420	−0.08			
	430	−0.70		430	+0.14			
	440	−0.66		440	+0.19			
	450	−0.64		450	+0.29			
	from area	−0.95		from area	−0.08			

un-ionised forms for different wavelengths do not depend on the concentration of the acid, then the change in the observed absorption coefficients should be due only to the change in the degree of ionisation of the indicator. In this instance the same values of C_B/C_{BH^+} should be obtained for all wavelengths. As the data of Table 2 show, the values of C_B/C_{BH^+} for 6-bromo-2,4-dinitroaniline in a particular medium depend on the wavelength chosen for the measurements. The explanation is that a change in the observed absorption coefficients for different wavelengths is due not only to the change in the C_B/C_{BH^+} ratio but also to the change in the absorption coefficients of the individual dual forms of the indicator. Such an effect is also observed for 2,4-dichloro-6-nitroaniline, and it is even more prominent with p-nitrodiphenylamine[20]. With o-nitroaniline, 2,4-dinitroaniline, 2,4,6-trinitroaniline, and p-nitroaniline at 25° the ratio C_B/C_{BH^+} is almost independent of the wavelength at $\lambda > \lambda_{max}$.[19]

In solutions of 2,4-dinitroaniline in concentrated phosphoric and polyphosphoric acids[15], there is a slight displacement of the absorption maximum and the absorptivity of this indicator varies under conditions where there is still no appreciable ionisation.

The concentration of a substance is characterised by the area under the curve plotted as absorption intensity against frequency. Therefore in measuring the acidity of a medium by the indicator method, even in instances where the absorption maximum of the indicator is not displaced by changing the acid concentration, integral intensities should be used. The measurement of integral intensities is rather laborious and is not always feasible. When there is the above-mentioned complication, the values of $\log(C_B/C_{BH^+})$ obtained from the intensity for maximum absorption agree with the values obtained from the area under the curve from the absorption maximum towards longer wavelengths. This is shown by the example of 6-bromo-2,4-dinitroaniline and 5-chloro-2-nitroaniline[19], where there is hardly any displacement of the absorption maximum. Table 2 gives the values of C_B/C_{BH^+} for 6-bromo-2,4-dinitroaniline calculated for different wavelengths and from the area under the absorption curve, taken from Vinnik and coworkers[19].

When it is impossible to use integral intensities in determining the indicator ratio C_B/C_{BH^+} then it is desirable to measure the intensity at the absorption maximum.

3. VALUES OF H_0 FOR AQUEOUS SOLUTIONS OF STRONG ACIDS AND OLEUM

The problems which related to the quantitative characteristic of acid media were discussed in detail in Shatenshtein's monograph[2]. Paul and Long[21] published a thorough review of work on the acidity of aqueous and non-aqueous solutions of acids in 1957, and subsequently papers appeared in which the values of H_0 were refined and the acidities of new solutions were measured. The present review only gives values of the acidity function for aqueous solutions of strong acids and oleum.

a. Sulphuric Acid

The acidity function of sulphuric acid was first measured in work by Hammett and Deyrup[1] published in 1932. The results of these authors for the region from dilute solutions up to 68% H_2SO_4 were repeatedly confirmed in later investigations[20,22,23], but the acidity function for more concentrated solutions was determined[1] with greater error, as the indicators used were benzalacetophenone and anthraquinone, which do not satisfy the requirements applicable for indicators. The indicators used by Jorgenson and Hartter[24] to measure the acidity function of sulphuric acid solutions

from 65 to 90% H_2SO_4 were: 2,6-dinitroaniline, 4-chloro--2,6-dinitroaniline, 2-bromo-4,6-dinitroaniline, 3-methyl--2,4,6-trinitroaniline, 3-chloro-2,4,6-trinitroaniline, and 3-bromo-2,4,6-trinitroaniline. For the same acid concentration range the observed difference in $\log(C_B/C_{BH^+})$ was satisfactorily constant between 2,4-dinitroaniline and 2,6-dinitroaniline, and also between 2,6-dinitroaniline and 4-chloro-2,6-dinitroaniline.

The data on the ionisation of 6-bromo-2,4-dinitroaniline obtained by Vinnik and coworkers [19] differ somewhat from those of Jorgenson and Hartter [24]. As we determined [19] the value of C_B/C_{BH^+} from the area under the absorption curve, these results are naturally more accurate. The acidity of acid solutions with >90% H_2SO_4 can be measured by using 3-methyl-2,4,6-trinitroaniline, 2,4,6-trinitroaniline, and *p*-nitrotoluene [25]. Jorgenson and Hartter [24] also propose 3-bromo-2,4,6-trinitroaniline and 3-chloro-2,4,6-trinitroaniline for this purpose. As the acid concentration is raised, the C_B/C_{BH^+} ratio for 3-bromo-2,4,6-trinitroaniline and 3-chloro-2,4,6-trinitroaniline falls more sharply than would be expected by the acidity of the medium measured by 3-methyl-2,4,6-trinitroaniline (from Jorgenson and Hartter's results [24]) and 2,4,6-trinitroaniline‡ (Vinnik and Ryabov [9]); the reason for this is still not clear. Possibly it is connected with errors in the measurements, or with the quantity $f_B f_{CH^+}/f_{BH^+} f_C$ not being constant for these substances.

Table 3 gives published [19] values of H_0 at 25° for aqueous solutions of sulphuric acid. The acidity function for sulphuric acid at elevated temperatures was measured by Gel'bshtein and coworkers [22] by a photometric method. Table 4 gives their results for the interval from 4% H_2SO_4 to 54% H_2SO_4 (the measurements were made with *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, and 2,4-dichloro-6-nitroaniline). The H_0 for more concentrated solutions of sulphuric acids are not given here for the following reasons. In addition to the indicators mentioned, 2,4-dinitroaniline (from 60.2 to 73.4% H_2SO_4), 6-bromo-2,4-dinitroaniline (from 78.0 to 89.5% H_2SO_4), and 2,4,6-trinitroaniline (from 97.1 to 99.6% H_2SO_4) were used [22]. pK_{BH^+} for the last two indicators cannot be determined by comparing $\log(C_B/C_{BH^+})$ since the acidity has not been measured by another indicator in the chosen ranges of H_2SO_4 concentrations. The ionisation regions of 2,4-dichloro-6-nitroaniline and 2,4-dinitroaniline overlap in the range 60.2–64% H_2SO_4. However, it is impossible to determine pK_{BH^+} for the latter indicator since the difference in $\log(C_B/C_{BH^+})$ for these substances depends significantly on the acid concentration.

TABLE 3. Acidity function of sulphuric acid at 25°.

H_2SO_4, %	H_0	H_2SO_4, %	H_0	H_2SO_4, %	H_0
1	+0.84	45	−2.95	92	− 9.33
3	+0.31	47	−3.13	94	− 9.59
5	−0.02	50	−3.41	96	− 9.88
8	−0.28	52	−3.60	98	−10.27
10	−0.43	55	−3.91	99	−10.57
12	−0.58	57	−4.15	99.1	−10.62
14	−0.73	60	−4.51	99.2	−10.66
16	−0.85	62	−4.82	99.3	−10.72
18	−0.97	65	−5.18	99.4	−10.77
20	−1.10	67	−5.48	99.5	−10.84
22	−1.25	70	−5.92	99.6	−10.92
25	−1.47	72	−6.23	99.7	−11.01
27	−1.61	75	−6.72	99.8	−11.18
30	−1.82	77	−7.05	99.85	−11.28
32	−1.96	80	−7.52	99.90	−11.43
35	−2.19	82	−7.84	99.95	−11.64
37	−2.34	85	−8.29	100	−11.94
40	−2.54	87	−8.60		
42	−2.69	90	−9.03		

TABLE 4. Acidity function of sulphuric acid at elevated temperatures*.

H_2SO_4, %	H_0			H_2SO_4, %	H_0		
	40°	60°	80°		40°	60°	80°
4	+0.19	+0.17	+0.15	28	−1.61	−1.63	−1.64
6	−0.11	−0.14	−0.13	30	−1.74	−1.76	−1.77
8	−0.29	−0.34	−0.35	32	−1.87	−1.89	−1.90
10	−0.44	−0.50	−0.52	34	−2.01	−2.03	−2.03
12	−0.58	−0.63	−0.66	36	−2.16	−2.15	−2.15
14	−0.69	−0.75	−0.79	38	−2.31	−2.31	−2.31
16	−0.82	−0.85	−0.89	40	−2.46	−2.47	−2.47
18	−0.95	−0.98	−1.01	44	−2.76	−2.78	−2.78
20	−1.07	−1.11	−1.14	48	−3.08	−3.09	−3.09
22	−1.21	−1.24	−1.26	50	−3.23	−3.24	−3.25
24	−1.34	−1.37	−1.39	54	−3.61	−3.59	−3.58
26	−1.47	−1.49	−1.51				

* In calculating H_0 for 40°, 60°, and 80° it was assumed that the quantity pK_{BH^+} for *p*-nitroaniline in sulphuric acid is the same as that in hydrochloric acid. The pK_{BH^+} for the other indicators were determined as usual. The values of pK_{BH^+} are given in Table 1.

b. Solutions of SO_3 in Sulphuric Acid

The acidity function of oleum has been measured by Brand and coworkers [25,26] and by Vinnik and coworkers [9]. In solutions with up to 36% SO_3 the following can serve as indicators: *p*-nitrotoluene, *p*-chloronitrobenzene, *p*-fluoronitrobenzene, *p*-bromonitrobenzene, *p*-butylnitrobenzene, *m*-nitrotoluene, and nitrobenzene. 2,4-Dinitrotoluene and the *m*-nitroanilinium ion [26] (addition of a second proton to *m*-nitroaniline) ionise in more concentrated solutions. Trinitrobenzene and 2,4,6-trinitrotoluene ionise only 20–30% in 65% oleum [26]. Table 5 gives values of H_0 for oleum solutions at 25°. There is no doubt that in dilute oleum the ionisation of the aforementioned indicators consists in the addition of a proton. In concentrated oleum the activity of sulphur trioxide rises sharply and the latter can be attached to the indicator as an aprotic acid. The indicator method for measuring acidity does not distinguish between protonation and ionisation by addition of an aprotic acid.

TABLE 5. Acidity function of oleum at 25°.

SO_3, %	$-H_0$	SO_3, %	$-H_0$	SO_3, %	$-H_0$
0.15	12.1	3.0	12.74	14	13.39
0.2	12.13	3.5	12.78	16	13.47
0.4	12.26	4.0	12.83	18	13.55
0.5	12.30	5.0	12.90	20	13.62
0.6	12.33	6.0	12.98	22	13.68
0.8	12.38	7.0	13.04	25	13.76
1.0	12.43	8.0	13.1	27	13.81
1.5	12.54	9.0	13.15	30	13.91
2.0	12.62	10.0	13.21	32	13.98
2.5	12.68	12.0	13.31	36	14.13

‡ The data on the ionisation of 2,4,6-trinitroaniline obtained by Jorgenson and Hartter [24] differ considerably from those of Vinnik and Ryabova [9].

More precise information about the ionisation mechanism of indicators in concentrated oleum could be obtained by studying the dependence of the rate of deuterium exchange with the hydrogen of the aromatic ring for the indicator (type RNO_2). It should be noted that in dilute oleum there is a marked rise in acidity with increase in SO_3 concentration. In more concentrated solutions the acidity of the medium increases in proportion to the activity of the sulphur trioxide.

c. Hydrochloric and Hydrobromic Acids

Hammett and Paul[27] measured the acidity function of aqueous solutions of hydrogen chloride from dilute solutions to 20% HCl, and their results were confirmed in later investigations[3,28]. The acidity function of more concentrated solutions has been measured[29,30]. The following indicators were used: aminoazobenzene; benzeneazodiphenylamine, *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, 5-chloro-2-nitroaniline, *p*-nitrodiphenylamine, 2,4-dichloro-6-nitroaniline, and 2,4-dinitroaniline. In solutions of acid where indicators with similar values of pK_{BH^+} overlap, a constant difference in $\log(C_B/C_{BH^+})$ for these indicators is observed satisfactorily.

Table 6 shows values of H_0 for aqueous solutions of HCl at 22–26°. Table 7 gives values of the acidity function for hydrochloric acid at 40°, 60°, and 80°, from Gel'bshtein and coworkers[28].

The acidity function of solutions of hydrobromic acid[30] at 25° was measured with the indicators: *p*-nitroaniline, *o*-nitroaniline, 5-chloro-2-nitroaniline, 2,4-dichloro-6-nitroaniline, and 2,4-dinitroaniline (Table 8).

d. Perchloric Acid

The acidity function of aqueous solutions of perchloric acid from 6% $HClO_4$ to 63.9% $HClO_4$ was measured by Hammett and Deyrup[1], using *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline, and *p*-nitroazobenzene. The last indicator overlaps with 4-chloro-2-nitroaniline and 2,4-dichloro-6-nitroaniline. However, it is impossible to calculate its pK_{BH^+} since the difference in $\log(C_B/C_{BH^+})$ for *p*-nitroazobenzene and other indicators changes with the concentration of the acid. Bonner and Lockhart[31] measured the acidity function of concentrated solutions (from 49.6 to 71.3% $HClO_4$) with 2,4-dinitroaniline and 2,4-dinitro-1-naphthylamine. For the same solutions of the acid the values of $\log(C_B/C_{BH^+})$ in these works differ by 0.25–0.28 units. The reason for this difference is still difficult to explain. In recent work by Yates and Wai[32] the acidity of aqueous solutions of perchloric acid at 25° was measured again over the range 4.9 to 78.6% $HClO_4$ using the indicators: *o*-nitroaniline, 4-chloro-2-nitroaniline, 2,5-dichloro-4-nitroaniline, 2-chloro-6-nitroaniline, 2,6-dichloro-4-nitroaniline, 2,4-dinitroaniline, 2,6-dinitroaniline, 4-chloro-2,6-dinitroaniline, 2-bromo-4,6-dinitroaniline, 3-methyl-2,4,6-trinitroaniline, and 3-bromo-2,4,6-trinitroaniline. The Hammett relation is observed by all the indicators mentioned. The results[32] for dilute solutions differ from the earlier data[1]. For example, the values of $\log(C_B/C_{BH^+})$

TABLE 6. Acidity function of aqueous solutions of HCl at 22–26°.

HCl, %	H_0	HCl, %	H_0
0.1	+1.56	16	−1.68
0.2	+1.36	18	−1.93
0.5	+0.81	20	−2.17
0.7	+0.62	22	−2.43
1.0	+0.4	24	−2.72
2.0	+0.17	26	−3.0
3.0	+0.03	28	−3.28
4.0	−0.17	30	−3.52
5.0	−0.33	32	−3.78
7.0	−0.61	34	−4.05
10	−0.95	36	−4.35
12	−1.17	38	−4.6
14	−1.40	−4,6	−4.99

TABLE 7. Acidity function of aqueous solutions of HCl at 40°, 60°, and 80°*.

HCl, wt. %	H_0		
	40°	60°	80°
0.5	+0.79	+0.80	—
1.0	+0.43	+0.38	—
1.5	+0.23	+0.18	—
2.0	+0.08	+0.02	—
3.0	−0.13	−0.21	−0.28
4.0	−0.3	−0.38	−0.34
5.0	−0.46	−0.54	−0.59
6.0	−0.62	−0.68	−0.73
8.0	−0,92	−0.89	−0.96
10	−1.05	−1.10	−1.16
12	−1.27	−1.33	−1.39
14	−1.50	−1.55	−1.61
16	−1.73	−1.77	−1.84
18	−1.95	−2,01	−2.05
19	−2.06	−2,12	−2.16

* Gel'bshtein and coworkers[28] determined the pK_{BH^+} of *p*-nitroaniline by a comparison of $\log(C_B/C_{BH^+})$ with the logarithm of the mean ionic activity $\log a_\pm$. In compiling this table, pK_{BH^+} for *p*-nitroaniline was calculated by comparison of $\log(C_B/C_{BH^+})$ with C_{HCl} in the interval 0.04–0.099 m. The pK_{BH^+} of *o*-nitroaniline and of 4-chloro-2-nitroaniline were determined in the usual way.

TABLE 8. Acidity function of aqueous solutions* of HBr at 22–26°.

HBr, %	H_0	HBr, %	H_0	HBr, %	H_0
0.1	+1.9	10	−0.35	37	−2.28
0.2	+1.6	12	−0.49	40	−2.26
0.3	+1.39	14	−0.64	42	−2.86
0.5	+1.22	16	−0.86	45	−3.24
0.8	+1.0	18	−0.89	47	−3.50
1.0	+0.90	20	−1.0	50	−3.95
1.5	+0.72	22	−1.13	52	−4.25
2.0	+0.56	25	−1.33	55	−4.76
3.0	+0.38	27	−1.47	56	−4.85
4.0	+0.23	30	−1.71	56.52	−4.90
6.0	−0.02	32	−1.83		
8.0	−0.20	35	−2.09		

* In calculating H_0, Vinnik and coworkers[30] used the values of the pK_{BH^+} for indicators given by Hammett and Paul[27]. In compiling this table, the pK_{BH^+} were calculated by comparing the values of $\log(C_B/C_{BH^+})$ for two indicators in the same solution. The pK_{BH^+} of *p*-nitroaniline were calculated by the formula:

$$pK_{BH^+} = -\log(C_B/C_{BH^+}) - \log m_{H_3O^+}$$

for the range of HBr concentrations 3.34×10^{-2}–0.158 m.

for *o*-nitroaniline for the same acid concentrations do not agree. According to Hammett and Paul the pK_{BH^+} of *o*-nitroaniline is more negative by 0.1 unit and the pK_{BH^+} of *p*-chloronitroaniline by 0.05 unit. Possibly this disagreement is connected with measurement errors. The results of Bonner and Lockhart and of Yates and Wai on the ionisation of these indicators agree satisfactorily. To obtain reliable values of pK_{BH^+} for the indicators it is necessary to assume information about the ionisation of strong bases which ionise in solutions where $H_0 = \log m_{H_3O^+}$. For this purpose *p*-nitroaniline can be used. The ionisation of this indicator has been measured[1] in rather concentrated solutions of perchloric acid ($C_{BH^+}/C_B > 10$). Unfortunately this indicator was not employed in the last investigations. Hammett and Deyrup[1] used a colorimeter and the other investigators[31,32] spectrophotometers, so that the results of the later works should be preferred. Table 9 gives the values of the acidity functions of aqueous solutions of perchloric acid.

e. Nitric Acid

In dilute aqueous solutions, nitric, phosphoric, methanesulphonic, and hydrofluoric acids are weak acids. However, concentrated solutions of these acids exhibit considerable catalytic activity in acid–base processes. An appreciable rise in the acidity of the medium is also observed in such solutions.

The acidity function for dilute and moderately concentrated solutions of nitric acid (up to 37.5% HNO_3) was measured by Hammett and Paul[27], using *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline. Dawber and Wyatt[17] measured the acidity over a wide range of concentrations from 0.12 to 99.4% HNO_3. In measuring the acidity of concentrated aqueous solutions of nitric acid, difficulties arose over the choice of indicators, owing to their instability in such media. For example, in acid solutions with >65% HNO_3, 2,4-dinitroaniline, *N*-methyl-2,4-dinitroaniline, 4-methyl-2,6-dinitroaniline, 4-chloro-2,6-dinitroaniline, 4-dinitrodiphenylamine, and 2,4-dinitrodiphenylamine react with the acid. In solutions with >37% HNO_3, they used 2,6-dichloro-4-nitroaniline, 2,4-dichloro-6-nitroaniline, *NN*-dimethyl-2,4,6-trinitroaniline, and 4,4′-dinitrodiphenylamine. The value of pK_{BH^+} of *p*-nitroaniline was determined by the equation

$$pK_{BH^+} = \log \frac{C_{BH^+}}{C_B} - \log m_{H_3O^+},$$

pK_{BH^+} for the other indicators, except *NN*-dimethyl-2,4,6-trinitroaniline, being determined as usual. The difference in $\log(C_B/C_{BH^+})$ for two indicators in the interval of their overlap agrees with a satisfactory constancy. *NN*-Dimethyl-2,4,6-trinitroaniline ionises to an appreciable extent, starting from 71.2% HNO_3. In more dilute solutions 2,4-dichloro-6-nitroaniline was used for the measurements. However, it was used for acidity measurements only up to 64.5% HNO_3 and therefore it is impossible to determine the pK_{BH^+} of *NN*-dimethyl-2,4,6-trinitroaniline in the usual way. The authors[17] assumed that at the same value of $\log(C_B/C_{BH^+})$ there should be the same value of H_0 in aqueous solutions of sulphuric and nitric acids. The acidity for the range 64.5–83.7% HNO_3 was examined for comparison of C_B/C_{BH^+} for *NN*-dimethyl-2,4,6-trinitroaniline in solutions of nitric and sulphuric acids. As already mentioned the indicator ratio for this substance changes anomalously in sulphuric acid. When allowance is made for this, there are grounds for assuming, as the authors themselves did[17], that for solutions with >64.5% HNO_3 there are still no reliable values for H_0. In the range 83.7–99.4% HNO_3 4,4′-dinitrodiphenylamine was used. The change in H_0 can be calculated from the change in its $\log(C_B/C_{BH^+})$ (see Table 10). To determine its pK_{BH^+} it is necessary to find indicators with the aid of which H_0 can be determined in the range 60–90% HNO_3.

Table 11 gives the values of H_0 for the HNO_3–H_2O system.

f. Phosphoric Acid and Polyphosphoric Acids

Heilbronner and Weber[33] measured the acidity function at 20° of aqueous solutions of phosphoric acid containing 0.6–85.5% H_3PO_4. The acidity function of such solutions and of more concentrated solutions at 20° and higher temperatures have been measured[28,34]. Downing and Pearson[15] measured the acidity function of solutions of polyphosphoric acids. There were no experimental difficulties

TABLE 9*. Acidity function of aqueous solutions of $HClO_4$ at 25° from published data[31,32].

$HClO_4$, %	H_0	$HClO_4$, %	H_0	$HClO_4$, %	H_0
5	+0.02	27	−1.40	52	− 3.81
8	−0.21	30	−1.59	55	− 4.30
10	−0.34	32	−1.73	57	− 4.64
12	−0.47	35	−1.95	60	− 5.23
14	−0.60	37	−2.10	62	− 5.68
16	−0.72	40	−2.37	65	− 6.46
18	−0.85	42	−2.57	68	− 7.19
20	−0.97	45	−2.89	70	− 7.75
22	−1.09	47	−3.12	75	− 9.23
25	−1.27	50	−3.51	78	−10.13

* In compiling the table it was assumed that pK_{BH^+} for *o*-nitroaniline is −0.29.

TABLE 10. Ionisation of 4,4′-dinitrodiphenylamine in nitric acid[17] at 20°.

HNO_3, %	$\log \frac{C_{BH^+}}{C_B}$	HNO_3, %	$\log \frac{C_{BH^+}}{C_B}$
83.7	−1.29	94.1	−0.62
85.6	−1.72	95.4	−0.43
87.7	−0.84	97.5	−0.24
90.5	−0.72	98.9	−0.07
93.0	−0.66	99.4	−0.02

TABLE 11. Acidity function of solutions of nitric acid in water at 20°.

HNO_3, %	H_0	HNO_3, %	H_0	HNO_3, %	H_0
0.2	+1.50	8.0	−0.49	35	−2.09
0.4	+1.17	10	−0.65	37	−2.22
0.5	+0.99	12	−0.80	40	−2.36
0.7	+0.89	14	−0.92	42	−2.47
1.0	+0.71	16	−1.05	45	−2.63
1.5	+0.49	18	−1.18	47	−2.73
2.0	+0.33	20	−1.31	50	−2.90
2.5	+0.2	22	−1.43	52	−3.0
3.0	+0.05	25	−1.59	55	−3.16
4.0	−0.1	27	−1.69	57	−3.28
5.0	−0.22	30	−1.85	60	−3.45
6.0	−0.31	32	−1.94	62	−3.59
				65	−3.78

in using the indicator method for work with dilute solutions of phosphoric acid but they did arise in measuring the acidity of concentrated solutions of P_2O_5 in water and especially in polyphosphoric acids. As is known, solutions of P_2O_5 in orthophosphoric acid, and also aqueous solutions of phosphorus pentoxide in water, close in composition to H_3PO_4, consist of mixtures of orthophosphoric, pyrophosphoric, and polyphosphoric acids[35]. Possibly, owing to the slow establishment of equilibrium different investigators worked with the same specified content of P_2O_5 in water but differing in the composition of the individual components. This can explain much of the disagreement in the values of H_0. To measure the acidity function of the P_2O_5–H_2O system, *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, 5-chloro-2-nitroaniline, *p*-nitrophenylamine, 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline, and 6-bromo-2,4-dinitroaniline were used. With 2,4-dinitroaniline there is a weak displacement of the absorption maximum[15], a shift which depends on the P_2O_5 concentration. While there is still no appreciable degree of ionisation in the solutions there is a significant change in the absorptivity of 2,4-dinitroaniline and because of this it is difficult to determine accurately the absorptivity of its un-ionised form. Table 12 gives the values of H_0 at 20° for solutions of P_2O_5 in water from published data[15,28,34]. The acidity function of solutions with from 43.45 to 72.85% P_2O_5 has been measured with 2,4-dichloro-6-nitroaniline colorimetrically[34] and with 2,4-dinitroaniline spectrophotometrically[15]. The results practically agree. The value of pK_{BH^+} for 2,4-dichloro-6-nitroaniline in phosphoric acid is -3.02 (in sulphuric acid pK_{BH^+} = -3.28; in hydrochloric acid, pK_{BH^+} = -3.33), and pK_{BH^+} of 2,4-dinitroaniline is -4.96 (in sulphuric acid pK_{BH^+} = -4.45; in hydrochloric acid pK_{BH^+} = -4.58). The reason for such a great difference in pK_{BH^+} is still difficult to explain.

g. Hydrofluoric Acid

The acidity function of solutions of hydrofluoric acid was measured by Bell and coworkers[36] from dilute solutions to 43% HF. The indicators used were: *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline. The acidity function for more concentrated solutions (right up to 100% HF) was measured by Kilpatrick and coworkers[37], who worked with optical cells made from polyfluorochloroethylene with sapphire windows. The measurements were made with *p*-nitrodiphenylamine (39.6–48.7% HF), 4-methyl-2,6-dinitroaniline (55.3% HF), 6-bromo-2,4-dinitroaniline (61.4–71% HF), anthraquinone (80.9–100% HF), and 2,4,6-trinitroaniline (98.13–100% HF). Unfortunately in this work solutions were chosen which do not ensure an overlap of indicators with similar pK_{BH^+}. Therefore it is impossible to determine the pK_{BH^+} of the indicators in this particular medium. The authors of this work[37] used values of pK_{BH^+} for aqueous solutions of sulphuric acid and because of this the values they give are approximate. Judging from their results dilute solutions of water in liquid hydrogen fluoride have an acidity close to that of dilute solutions of water in sulphuric acid. This is evident from the values of C_B/C_{BH^+} for 2,4,6-trinitroaniline (see Table 13).

Table 14 gives values of H_0 for solutions of hydrogen fluoride in water over the range 2–42.7% HF, after Bell and coworkers[36].

h. Methanesulphonic Acid CH_3SO_3H

The acidity of aqueous solutions of methanesulphonic acid at 25° in the range 0–100% was measured by Bascombe and Bell[20]. No appreciable change in the ratio C_B/C_{BH^+} with wavelength is observed for the indicators listed below. The acidity was measured: from 3 to 13.9% acid with *p*-nitroaniline; from 17 to 21.9% with *o*-nitroaniline, from 25.5 to 54.5% acid with 4-chloro-2-nitroaniline, and from 61.5 to 80.6% acid with 2,4-dichloro-6-nitroaniline. The last range of acid concentrations partly overlaps with 4-methyl-2,6-dinitroaniline, the ionisation of which was measured in 74.9–85.2% acid. In 88.9–100% acid the C_B/C_{BH^+} ratio was measured for 6-bromo-2,4-dinitroaniline. To calculate H_0 the authors assumed that for *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline, pK_{BH^+} in methanesulphonic acid is the same as in hydrochloric and sulphuric acids.

TABLE 12*. Values of H_0 for the P_2O_5–H_2O system at 22–26°.

H_3PO_4, %	P_2O_5, %	H_0	H_3PO_4, %	P_2O_5, %	H_0	P_2O_5, %	H_0
10	7.24	+0.65	57	41.3	−1.63	76	−5.12
12	8.7	+0.53	60	43.5	−1.83	77	−5.26
14	10.1	+0.44	62	44.9	−1.97	78	−5.42
16	11.6	+0.34	65	57.1	−2.19	79	−5.58
18	13.0	+0.25	70	50.7	−2.53	80	−5.72
20	14.5	+0.17	72	52.2	−2.69		
22	15.9	+0.09	75	54.3	−2.90		
24	17.4	0	78	55.5	−3.14		
26	18.8	−0.07	80	58	−3.30		
28	20.3	−0.16	82	59.4	−3.42		
30	21.7	−0.24	85	61.6	−3.62		
32	23.2	−0.33	87	63.1	−3.78		
35	25.4	−0.47	90	65.2	−4.01		
37	26.8	−0.55	92	66.7	−4.15		
40	29.0	−0.69	94	68.2	−4.29		
42	30.4	−0.78	96	69.6	−4.41		
45	32.6	−0.94	98	71.0	−4.52		
47	34.1	−1.05	99	71.7	−4.59		
50	36.2	−1.20	100	72.4	−4.66		
52	37.7	−1.32		73	−4.71		
55	39.9	−1.51		74	−4.85		
				75	−4.98		

* In compiling the table, pK_{BH^+} for *p*-nitroaniline was taken as +1.0; pK_{BH^+} for the other indicators were determined in the usual way.

TABLE 13. Ionisation of 2,4,6-trinitroaniline in hydrofluoric acid.

Concentration of H_2O in HF, M	$\log \frac{C_B}{C_{BH^+}}$	Concentration of H_2O in HF, M	$\log \frac{C_B}{C_{BH^+}}$
<0.001	−0.79	0.63	+0.07
<0.01	−0.55	0.83	+0.29
0.12	−0.18	0.87	+0.32
0.38	−0.06	0.89	+0.3
0.50	+0.1	1.03	+0.55

TABLE 14. Acidity function of aqueous solutions of hydrofluoric acid at 25°.

HF, %	H_0	HF, %	H_0
2	+1.33	20	−0.37
3	+1.09	22	−0.52
4	+0.98	25	−0.76
5	+0.87	30	−1.11
8	+0.57	32	−1.25
10	+0.37	35	−1.47
12	+0.21	37	−1.62
15	−0.01	40	−1.88
17	−0.15	42,7	−2.10

TABLE 15. Acidity function of aqueous solutions of methanesulphonic acid at 25°, after Bascombe and Bell[20].

CH_3SO_3H, %	H_0	CH_3SO_3H, %	H_0	CH_3SO_3H, %	H_0
3	+0.43	35	−1.19	70	−3.57
5	+0.17	40	−1.41	75	−4.04
10	−0.20	45	−1.67	80	−4.56
15	−0.43	50	−2.0	85	−5.37
20	−0.60	55	−2.34	90	−6.31
25	−0.76	60	−2.71	95	−7.11
30	−0.97	65	−3.11	100	−7.86

The values of pK_{BH^+} of 2,4-dichloro-6-nitroaniline and 6-bromo-2,4-dinitroaniline were calculated by extrapolation. It appeared that here pK_{BH^+} for these substances greatly differs from the values for sulphuric acid obtained by direct measurements. As pK_{BH^+} were not determined by overlap of the same ranges of acid concentrations for different indicators the values of H_0 for the methanesulphonic acid–water system (Table 15) must be considered only approximate. These results show that concentrated aqueous solutions of methanesulphonic acid exhibit strongly acid properties.

i. Solutions of DCl and D_2SO_4 in D_2O

In some kinetic investigations solutions of acids in deuterium oxide D_2O are used. It is therefore necessary to have information about the values of H_0 for such systems. Högfeldt and Bigeleisen[38] measured the acidity function for solutions of DCl in D_2O for the range 10^{-4}–1 M DCl and of D_2SO_4 in D_2O for the range 10^{-4}–12 M D_2SO_4 at 22° ± 2°. Fourteen indicators were used for the measurements. It appeared that at the same molarity of the acid the acidity function was the same (within the limits of error of the measurements) for solutions of HCl in H_2O and DCl in D_2O (from 10^{-4} to 1 M) and for solutions of H_2SO_4 in H_2O and of D_2SO_4 in D_2O (from 10^{-1} to 12 M). The acidity was not measured for more concentrated solutions of the acids in D_2O.

pK_{BH^+} for solutions in D_2O is greater than for solutions in H_2O. pK_{BH^+} in D_2O is greater than in water for aminoazobenzene, *m*-nitroaniline, 2,4-dichloroaniline, benzeneazodiphenylamine, *p*-nitroaniline, diphenylamine, *o*-nitroaniline, and 4-chloro-2-nitroaniline by 0.5–0.6 unit; for *p*-nitrodiphenylamine, by 0.27 unit; and for 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline, and 4-methyl-2,6-dinitroaniline by almost 0.4 unit.

4. ACCURACY OF MEASUREMENTS OF H_0

In the measurements of acidity function there are the following sources of error: (a) the determination of the concentration of the acid; (b) the determination of the indicator ratio C_B/C_{BH^+}; (c) the determination of the value of pK_{BH^+} for the indicator.

Usually, the concentration of aqueous solutions of strong acids is determined either by alkalimetric titration or by electrical conductivity. The electrical conductivity method[39] is used mainly for determining the concentration of sulphuric acid in solutions with >99% H_2SO_4. In alkalimetric titration the error does not exceed 0.1–0.05%. On altering the concentration of strong acids by 1% the acidity function changes by 0.1–0.15 unit in moderately concentrated and by 0.3 unit in extremely dilute solutions. Hence the error in measuring the acid concentration introduces 0.02–0.03 unit into the error in H_0. In measuring H_0 for sulphuric acid in the range 99.5–100% where H_0 changes by 0.3–0.5 unit per 0.1% acid, the error due to the inaccuracy in determining the H_2SO_4 concentration does not exceed 5×10^{-3}–0.01 unit. In this region the accuracy of determining the concentration by electrical conductivity is ±0.001%. In using spectrophotometry H_0 is frequently determined with an accuracy of ±0.01–0.02 unit[29]. However, in some instances an accuracy of ±0.003 is attained, when C_B/C_{BH^+} is determined at several wavelengths[9].

A more significant error is the measurement of the pK_{BH^+} of indicators. This quantity depends on the quantity of indicator used to measure H_0 of the solutions in which the indicator concerned ionises. The error in determining pK_{BH^+} of the first indicator (the strongest base) is made up of the errors in determining the concentration of the acid and $\log(C_B/C_{BH^+})$, since pK_{BH^+} is calculated by the equation:

$$(pK_{BH^+})_1 = -\log C_{H_3O^+} + \log \frac{C_B}{C_{BH^+}}.$$

The error $\Delta(pK_{BH^+})_1 = \pm(0.03-0.04)$ unit.

The quantity pK_{BH^+} of the second indicator, which is a rather weak base, is determined by the equation:

$$(pK_{BH^+})_2 = (pK_{BH^+})_1 + \log\left(\frac{C_B}{C_{BH^+}}\right)_2 - \log\frac{C_B}{(C_{BH^+})_1},$$

$$\Delta(pK_{BH^+})_2 = \Delta(pK_{BH^+})_1 + 2\Delta\log\frac{C_B}{C_{BH^+}} \simeq \pm(0.05-0.08)\text{ unit.}$$

For the third indicator:

$$\Delta(pK_{BH^+})_3 = \Delta(pK_{BH^+})_2 + 2\Delta\log\left(\frac{C_B}{C_{BH^+}}\right).$$

The error $(pK_{BH^+})_3$ amounts to ±(0.07–0.12) unit. The error in determining the pK_{BH^+} of subsequent indicators will be increased by ±(0.02–0.04) unit. The error in H_0 is the sum of the errors in pK_{BH^+}, $\log(C_B/C_{BH^+})$, and the acid concentration. When, for example, three indicators are needed to measure H_0 in a particular solution, then ΔH_0 = = ±(0.08–0.13) unit. When there are nine indicators, ΔH_0 = = ±(0.17–0.34) unit. This number of indicators is required in measuring the acidity of sulphuric acid from extremely dilute solutions to 100% H_2SO_4, where H_0 changes by 12–13 units. In practice in kinetic investigations narrower intervals are used, amounting to 3–5 units of the H_0 scale. In such an instance there is essentially no absolute error in the value of H_0 and the difference in the errors in measuring H_0 for the start and end of the interval. For the mentioned interval of 3–5 units, the error amounts to ±(0.08–0.13) unit), which is fully acceptable for kinetic investigations§. Table 1 does not give the errors in measurements for each indicator separately. The errors can be evaluated from what has been stated above. The stated experimental errors are also not given in the tables listing H_0 for acids. In dilute solutions the accuracy of these quantities is greater in dilute solutions than in concentrated. In each specific instance the error in H_0 is readily evaluated.

§ The errors in determining H_0 were calculated for instances when Hammett's hypothesis of an equality in the ratio of the coefficients for un-ionised and ionised forms of the substance is strictly obeyed.

5. PHYSICAL SIGNIFICANCE OF THE CONCEPT OF "ACIDITY OF THE MEDIUM"

The increase in the acidity of the medium $a_{H^+}(f_B/f_{BH^+})$ as the concentration of the acid in the solution is raised can be related to the change in the concentration of protons C_{H^+}, the activity coefficient of the protons f_{H^+}, and the ratio of the activity coefficients f_B/f_{BH^+} of the indicator. Since the energy of interaction of a proton with water is ~ 200 kcal $\times$ $\times$ mole^{-1}, the concentration of free protons in aqueous solutions of acids is vanishingly small; the protons are present as hydroxonium ions H_3O^+. It is therefore necessary to relate the acidity of aqueous solutions with the properties of H_3O^+ ions and with the f_B/f_{BH^+} ratio.

In aqueous solutions of acids, hydroxonium ions and molecules of the undissociated acids HA, which are in equilibrium with one another, can donate protons:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-. \qquad (8)$$

The ionisation of substance B can be expressed by the equations:

$$B + H_3O^+ \rightleftharpoons BH^+ + H_2O, \qquad (9)$$

$$B + HA \rightleftharpoons BH^+ + A^-. \qquad (10)$$

When the ionisation of B is represented by Eqns. (9) or (10) then the acidity is expressed thus:

$$h_0 = a_{H^+}\frac{f_B}{f_{BH^+}} = \frac{a_{H_3O^+}}{a_{H_2O}}\frac{f_B}{f_{BH^+}}; \qquad h_0 = \frac{1}{K_4}\frac{a_{HA}}{a_{A^-}}\frac{f_B}{f_{BH^+}},$$

where K_4 is the equilibrium constant for the ionisation of the acid by Eqn. (8):

$$K_4 = \frac{a_{HA}\,a_{H_2O}}{a_{A^-}\,a_{H_3O^+}}.$$

In non-aqueous solutions the ionisation of acids involves the transfer of a proton from the acid HA to the solvent molecule. In alcoholic solutions, alkoxonium ions ROH_2^+ are formed; in ethereal solutions, the ions $RR'O^+H$. In pure acids the ions are formed during autoprotolysis:

$$2HA \rightleftharpoons A^- + H_2A^+.$$

The acidity of the non-aqueous solutions should be related to the properties of the ions of type ROH_2^+, $RR'O^+H$, and H_2A^+ and to the ratio f_B/f_{BH^+} of the indicators used to measure H_0. It is well known that even highly concentrated aqueous solutions of hydrochloric acid [40,41] are completely dissociated. Perchloric acid [42,43] is also completely dissociated in aqueous solutions of moderate concentration (up to 6 M). The concentration of hydroxonium ions in such solutions equals the total concentration of the acid. In concentrated aqueous solutions of sulphuric [10,11] and nitric [44] acids there is incomplete dissociation. The concentration of H_3O^+ ions, anions, and undissociated HA molecules in such solutions can be determined from the Raman spectra, by infrared spectra, and by the NMR method. Acids such as phopshoric and hydrofluoric are weakly dissociated even in dilute aqueous solutions.

It is easy to conclude that the acidity of concentrated solutions increases much more strongly than the concentration of H_3O^+ ions. For solutions with completely dissociated acids with a range of concentrations of 1–10 M, $C_{H_3O^+}$ increases tenfold, and the acidity of the medium by a few orders of magnitude. Evidently the chief reason for the change in H_0 is not the change in $C_{H_3O^+}$, but the change in activity coefficients. The activity coefficients of individual ions, in principle, cannot be measured by thermodynamic methods. The acidity h_0 includes the activity coefficient of the un-ionised form of the indicator f_B, which can be measured indirectly.

The demonstration of the dependence of f_B for indicators on the acid concentration allows us to understand the physical significance of acidity h_0.

Until recently information about the dependence of f_B for indicators on the concentration of strong acids was limited solely to aqueous solutions of sulphuric acid. Figs. 2 and 3 show the dependence of f_B for certain indicators on sulphuric acid concentration from published data [45-47]. In dilute solutions the activity coefficients of the un-ionised form f_B are almost constant. On increasing the acid concentration the quantities f_B for various indicators change differently for different indicators. For *o*-nitroaniline, f_B remains constant almost up to 25% H_2SO_4, and then falls.

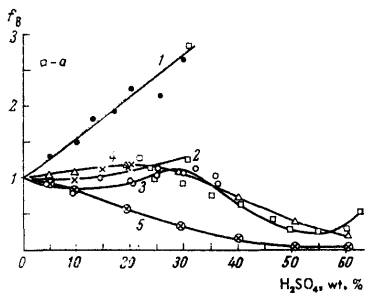

Fig. 2. Dependence of the activity coefficients f_B of the un-ionised form of the indicators on sulphuric acid concentration:
1) diphenylamine; 2) *p*-nitroaniline; 3) *o*-nitroaniline; 4) 2,6-dichloro-4-nitroaniline;
5) 2,4,6-trinitroaniline; □ experiments on the distribution of the substance between two phases; other experiments, by solubility.

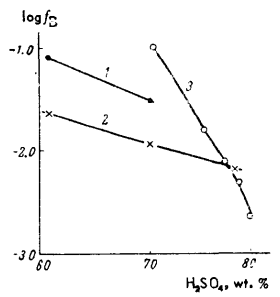

Fig. 3. Dependence of the activity coefficients f_B of the un-ionised form of the indicators on the sulphuric acid concentration:
1) 2,4-dinitroaniline; 2) 2,4,6-trinitroaniline; 3) *p*-benzoylbiphenyl. For *p*-benzoylbiphenyl instead of f_B we give the quantity $(1 + h_0/k_{BH^+})/S$ which is proportional to f_B. In this, S is the solubility of the substance in acid of the specified concentration.

For 2,4-dinitroaniline and 2,4,6-trinitroaniline there is only a decrease in f_B with increasing acid concentration, and the degrees of change of f_B are different. With *p*-nitroaniline, f_B remains constant at first and then rises slowly. With diphenylamine there is a rise in f_B, starting from dilute acid solutions. For these indicators Hammett's hypothesis of the equality of the ratios of activity coefficients of the ionised and un-ionised forms of the indicator is satisfied:

$$\frac{f_B}{f_{BH^+}} = \frac{f_C}{f_{CH^+}} = \frac{f_D}{f_{DH^+}}. \qquad (11)$$

In the general example this ratio should depend on the composition of the solution. Assume that on going from a dilute solution of sulphuric acid to solution N this ratio changes m times, and the coefficients f_B, f_C, and f_D change b, c, and d times respectively. Then:

$$f_{BH^+} = \frac{b}{m}; \quad f_{CH^+} = \frac{c}{m}; \quad f_{DH^+} = \frac{d}{m}.$$

Hammett's relationship is also observed during the ionisation of an already protonated base[48] and during the protonisation of anions, for example, of picric acid[50,51]:

$$\frac{f_B}{f_{BH^+}} = \frac{f_{BH^+}}{f_{BH_2^{2+}}} = \frac{f_{A^-}}{f_{AH}},$$

where f_{AH} and f_{A^-} are the activity coefficients of the acid and its anion. When in solution N we have $f_B = b$ and $f_{AH} = a$, then:

$$f_{BH_2^{2+}} = \frac{b}{m^2} \text{ and } f_{A^-} = ma.$$

Consequently, when the value of relationship (11) depends on the solution composition, then in comparison with the activity coefficient of the un-ionised form, the activity coefficient of the singly-charged positive ion changes $1/m$ times; that of a doubly-charged positive ion $1/m^2$ times, and that of a singly-charged negative ion, m times.

An activity coefficient characterises the change in free energy of the substance. When relationship (11) depends on the composition of the solvent, then it can be taken that the change in free energy of the ion is the sum of two parts. One part (ΔF_1) equals the change in free energy of the un-ionised species; the other part (ΔF_2) is determined solely by the charge of the ion and does not depend on its structure and chemical composition. The substances for which relationship (11) is observed are usually large polyatomic molecules. In solutions with a high concentration of ions they are polarised. The substances investigated for which Hammett's hypothesis is obeyed contain such functional groups as amino, nitro, carbonyl, etc. On the basis of what has been said above, it is to be expected that the addition of a proton to various functional groups has the same effect on the activity coefficient of the ionised molecule. Moreover, in substances with such functional groups there is a marked change in the activity coefficient f_B with change in the acid concentration. In this connection it can be assumed that these particular groups are mainly responsible for the change in the activity coefficient of the un-ionised molecules. Undoubtedly, the acquisition of a charge is reflected in the properties of all the molecules as a whole, and in particular of the atoms of the functional group bearing the charge. When the contribution of the charge to the free energy of the ionised molecule is large then it significantly changes the properties of all the atoms of the molecule and in particular the atoms of the charged functional group. Here it is difficult to suggest that the change in free energy represents the sum of two independent terms, as it should be were f_B/f_{BH^+} dependent on the solution composition. When the effect of the charge is small, then the change in free energy of the ion can be expressed as the sum ($\Delta F_1 + \Delta F_2$) and the contribution of the charge ΔF_2 to this sum can be neglected.

Hence we come to the conclusion[46] that the ratio f_B/f_{BH^+} is independent of the solvent composition and equals unity, as is assumed for dilute aqueous solutions.

The acidity of the medium equals the activity of the protons $h_0 = a_{H^+}$.

Rybkin and Shevchenko[52] measured the compensating effect of the cell for aqueous solutions of hydrogen chloride and of solutions of HCl in water saturated with surface-active acids (hexanoic and enanthic) and alcohols (heptyl and nonyl). The compensating effects of the cell of type:

$$\underset{(I)}{H_2 \mid \text{acid} \mid} \text{ air } \underset{(II)}{\mid \text{acid} \mid H_2},$$

depend considerably on the state of the surface of the investigated (I) and standard (II) solutions. The surface adsorption potential of hydrogen chloride in aqueous solutions is suppressed by additions of pentanol[49]. Surface-active substances are added to balance the surface properties of the solutions. Since their solubility is not high it can be considered that they do not change the acidity of the test solutions. In solutions saturated with surface-active alcohols there is satisfactory agreement of the measured values of $\log a_{H^+}$ with the acidity function H_0. These experiments also show the independence of f_B/f_{BH^+} on the concentration of a strong acid in aqueous solution. The view that the ratio f_B/f_{BH^+} is constant in aqueous solutions of strong acids was expressed by Gutbezahl and Grunwald[53] in 1953. It is evident that the equality of the acidity of the medium and the activity of the protons does not mean in the least that in all instances Hammett's relationship should be observed. An example of the non-observance of this relation was given on p. 806. Hammett's relation is also not observed in instances when the ionic and un-ionised forms differ significantly in their structure, as happens in the ionisation of cyanocarboxylic acids[50].

6. RELATION BETWEEN THE ACIDITY OF THE MEDIUM AND THE THERMODYNAMIC ACTIVITY OF WATER

In aqueous solutions in which strong acids are completely ionised, there are anions and water molecules in addition to the hydroxonium ions. In such systems the properties of the H_3O^+ ions are determined by the properties of water and the anions A^-. If the conclusion about the independence of the ratio f_B/f_{BH^+} and the acid concentration is correct, then:

$$h_0 = \frac{1}{K_4}\frac{a_{HA}}{a_{A^-}} = \frac{a_{HA}}{K_4 C_{A^-} f_{A^-}}, \qquad (12)$$

where C_{A^-} is the concentration of the anions and f_{A^-} the activity coefficient of the anions of the acid.

For hydrochloric, hydrobromic, perchloric, and nitric acids the standard state is chosen in such a way that the constant K_4 equals unity. For these acids:

$$h_0 = \frac{a_{HA}}{C_{A^-} f_{A^-}}. \qquad (13)$$

Hydrochloric[40,41] and perchloric[42] acids are completely dissociated even in highly concentrated aqueous solutions

and the concentration of the anions equals the total concentration of the acid. Apparently, hydrobromic acid is also completely dissociated in concentrated solutions. It is well known that a molecule of water combined with a proton is spectroscopically distinct from the remaining molecules of water in aqueous solution[54]. Molecules of water entering into the solvate sheaths of the anions and H_3O^+ ions apparently differ little from the remaining water molecules present in the solution. To the first approximation it can be assumed that the concentration of water molecules in an aqueous solution equals the difference between the stoichiometric concentration of water and the concentration of H_3O^+ ions. Therefore it is sensible to compare the values of f_A- for solutions with the same molality. The activity coefficients of the anions can be calculated by Eqn. (13).

To calculate the activity coefficient f_A- for solutions of nitric acid in water, allowance must be made for the degree of dissociation of the acid. The degree of dissociation of HNO_3 in water is taken from Young and coworkers[44]. In dilute solutions of sulphuric acid there are SO_4^{2-} and HSO_4^- anions. The standard state for solutions of H_2SO_4 in water is chosen in such a way that the activity coefficients of the H_3O^+ ions and SO_4^{2-} anions equal unity in extremely dilute solutions. In concentrated solutions of the acid the SO_4^{2-} concentration is low[10,11] and the ionised acid is present as HSO_4^- anions. Then the equilibrium constant K_4 does not equal unity. For sulphuric acid the product $K_4 f_A$- can be calculated. Table 16 gives the activity of the anions of aqueous solutions: from 0.1 m to 12 m for HCl and HBr, from 0.5 m to 12 m for $HClO_4$, from 0.1 m to 10 m for HNO_3, and the values of $K_4 f_{HSO_4^-}$ for sulphuric acid solutions in the range 0.5–12 m.

As Fig. 4 shows, in the range from 1 m to 9 m the change in the acidity function H_0 is almost the same for aqueous solutions of HCl, HBr, $HClO_4$, and H_2SO_4¶. Since the activities of the anions change differently in this range it can be concluded that the change in $h_0/C_{H_3O^+}$ is connected with a change in the solvation of the hydroxonium ion and not with a change in a_A-.

With a decrease in the number of water molecules adjacent to one hydroxonium ion, the acidity rises. The

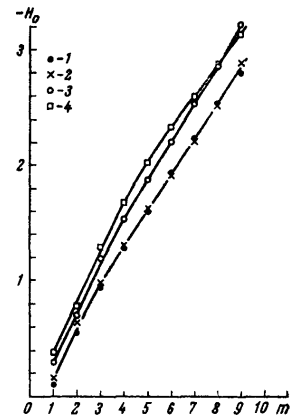

Fig. 4. Dependence of H_0 on the molar [presumably molal [Ed. of Translation)] concentration m of the strong acids: 1) HCl; 2) HBr; 3) $HClO_4$; 4) H_2SO_4.

activity of water in the solution is connected with the properties of the hydroxonium ion and the anion. In those instances where the activity of the anions change similarly for a change in the concentration of the acids it can be expected that at the same values of the activity of water a_{H_2O} the values of the acidity will be almost the same†. Table 17 gives the values of H_0 at the same activities of water. For solutions of sulphuric (from 11 to 57.8% H_2SO_4) and perchloric (from 11.3 to 54.6% $HClO_4$) acids, where the activity of water changes from 0.85 to 0.20, there are almost the same values of H_0 at the same activities of water.

Starting from solutions in which the activity of water < 0.45 the acidity of the medium for HCl, HBr, $HClO_4$, and H_2SO_4 is almost the same for the same values of a_{H_2O}. In such solutions the activities of the anions differ significantly. The activity coefficients of the ClO_4^- and HSO_4^- anions rise considerably and those of Cl^- and Br^- remain

¶ This first received attention from Bascombe and Bell[59].

† Wyatt[60] and Högfeldt[61] have compared values of H_0 and a_{H_2O} for various acids.

TABLE 16. Logarithms of the activity coefficients of the anions of hydrochloric, hydrobromic, perchloric, sulphuric, and nitric acids as a function of the concentration of the acid in aqueous solutions*.

Acid	Function	Molality of the acid 0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11	12
HCl	$\log \frac{a_{HCl}}{h_0}$	−1.22	−0.62	−0.28	+0.06	+0.25	+0 40	+0.54	+0.64	+0.74	+0.93	+0 91	+0.97	+1.06	+1.07
	$\log f_{Cl^-}$	−0.22	−0.32	−0.26	−0.24	−0.24	−0.20	−0 16	−0.14	−0.1	−0.03	−0 04	−0.03	+0.02	−0.01
HBr	$\log \frac{a_{HBr}}{h_0}$	−1.19	−0.57	−0.03	+0.11	+0.42	+0.54	+0.66	+0.77	+0.83	+0.90	+0,96	+0.97	+1.06	+1.12
	$\log f_{Br^-}$	−0.19	−0.27	−0.27	−0.19	−0.06	−0.06	−0.04	−0.01	+0.01	0.0	0,0	−0.03	+0.02	+0.04
$HClO_4$	$\log \frac{a_{HClO_4}}{h_0}$	—	−0.8	−0.47	−0.15	+0.01	+0.31	+0.51	+0.71	+0.8	+1.08	+1.26	+1.42	+1.58	+1.75
	$\log f_{ClO_4^-}$	—	−0.5	−0.47	−0.45	−0.47	−0.29	−0.19	−0.07	−0.04	+0.18	+0.31	+0.42	+0.54	+0.67
H_2SO_4	$\log \frac{a_{H_2SO_4}}{h_0}$	—	−2.78	−2.41	−2.07	−1.81	−1.59	−1.39	−1.18	−0.96	−0.78	−0.68	−0.53	−0.43	−0.32
	$\log f_{HSO_4^-} k_4$	—	−2.48	−2.41	−2.37	−2.29	−2.19	−2.09	−1.96	−1.80	−1.68	−1.60	−1.53	−1.47	−1.40
HNO_3	$\log \frac{a_{HNO_3}}{h_0}$	−1.28	−0.84	−0.58	−0.36	−0.29	−0.12	−0.06	−0.03	+0.01	—	—	−0.22	—	—
	$\log f_{NO_3^-}$	−0.28	−0.54	−0.53	−0.66	−0.75	−0.69	−0.71	−0.73	−0.73	—	—	−0.60	—	—

* The activities of the acids were taken from published works: hydrochloric[55], hydrobromic[30], perchloric[56], sulphuric[57], nitric[58]. In calculating $f_{NO_3^-}$ the degree of dissociation of nitric acid[44] was taken into account.

TABLE 17*. Values of H_0 for aqueous solutions of sulphuric, hydrochloric, hydrobromic, nitric, and phosphoric acids having the same activity of water at 25°.

a_{H_2O}	H_0					
	H_2SO_4	HCl	HBr	$HClO_4$	HNO_3	H_3PO_4
0.95	−0.51	−0.35	—	−0.42	−0.51	—
0.9	−0.95	−0.68	—	−0.89	−0.96	—
0.85	−1.30	−1.0	—	−1.23	−1.27	—
0.8	−1.59	−1.30	—	−1.46	−1.52	—
0.75	−1.82	−1.56	—	−1.68	−1.76	—
0.7	−2.04	−1.71	—	−1.91	−1.92	—
0.65	−2.31	−1.97	—	−2.12	−2.08	—
0.60	−2.42	−2.15	—	−2.32	−2.33	—
0.55	−2.59	−2.36	—	−2.52	−2.45	—
0.50	−2.37	−2.58	—	−2.71	−2.58	−1.97
0.45	−2.99	−2.83	—	−2.93	−2.75	−2.17
0.40	−3.21	−3.21	—	−3.15	−2.91	−2.34
0.35	−3.40	−3.35	—	−3.37	−3.11	−2.53
0.3	−3.64	−3.63	−3.74	−3.63	−3.31	−2.71
0.25	−3.90	−3.91	−3.95	−3.89	−3.52	−2.90
0.2	−4.25	−4.27	−4.2	−4.19	−3.78	−3.13
0.15	−4.61	−4.66	−4.5			−2.34
0.1	−5.1	−4.9				−3.60

* The activities of water a_{H_2O} in acids were taken from published data: sulphuric acid[57]; hydrochloric acid[41]; hydrobromic acid[41]; perchloric acid[58]; nitric acid[58]; phosphoric acid[62].

almost constant. This suggests that in solutions with >8–9 m acid the change in the activity of the anion is weakly reflected in the change in the activity of water. On the other hand, even a slight decrease in the activity of water in concentrated solutions of acid is linked with a significant increase in the activity coefficient of the oxygen-containing anions ClO_4^- and HSO_4^-. On comparing solutions of strongly and weakly dissociated acids with the same activities of water, the acidity is much less for weak acids than for strong acids. For example, for solutions with a water activity of 0.2, the acidity function for strong acids is $H_0 = -4.25$, for nitric acid $H_0 = -3.78$, and for phosphoric acid $H_0 = -3.13$. This can be explained by the strong hydration of the undissociated molecules of a weak acid.

It is interesting to note that in the dissolution of anhydrous hydrogen chloride in concentrated phosphoric acid containing 80% H_3PO_4, the acidity of the medium rises as the concentration of water in the solution decreases. At the same time the activity of the Cl^- anion remains almost constant[63]. A slight change in the activity coefficients of Cl^- in aqueous solutions and in solutions in phosphoric acid and also of Br^- in aqueous solutions shows the slight solvating ability of these ions.

In sulphuric acid solutions with >94% H_2SO_4‡, there is a relation found by Brand[25]:

$$-\log\frac{C_{H_2SO_4}}{C_{HSO_4^-}} + \log k = H_0, \qquad (14)$$

where k is a constant.

‡ It has been assumed[25,64] that in sulphuric acid with > 90% H_2SO_4, all the water is present as H_3O^+:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-.$$

The concentration of the undissociated H_2SO_4 molecules was calculated as the difference between the initial concentrations of acid and water. Then Eqn. (14) is correct in the range 90–99% H_2SO_4. However, from the spectroscopic data[11], it follows that in solutions where the acid concentration is < 94%, the concentration of HSO_4^- anions is less than the concentration of water in the initial acid.

In such solutions the change in activity of the sulphuric acid equals the change in the mole fraction of the undissociated molecules in solution. When the concentration of the anions in Eqn. (14) is expressed by mole fraction, then it is found that $f_{HSO_4^-}$ is constant in the range from 94 to 99% H_2SO_4. In solutions where the H_2SO_4 concentration <94%, considerable numbers of ion pairs are present in equilibrium with the H_2SO_4 molecules[11].

The chemical shifts of the NMR protons reflect the change in the acidity of the medium. The chemical shifts of the NMR protons depend on the nature and concentration of the acids[65]. The acidity function and also the value of $\log(h_0 a_{H_2O})$ for hydrochloric, perchloric, sulphuric, and nitric acids are linearly related to the chemical shift σ. However, the slope of the straight line in the coordinates: $[H_0; \sigma]$ or $[\log(h_0 a_{H_2O}); \sigma]$ depends on the nature of the anion. It changes in the following sequence: $HClO_4 > HCl > H_2SO_4 > > HNO_3$.

As mentioned above, the change in the activity of the anion has little effect on the acidity h_0. The existence of a relation between proton shift and the nature of the anion at the same values of H_0 is evidence of the considerable effect of the anion on the screening of the proton in aqueous solutions.

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TAUTOMERIC TRANSFORMATIONS OF PHENOLS

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1. INTRODUCTION

Problems of the tautomerism of organic compounds are at present of interest to many research workers[1]. Even in the most familiar type of tautomerism (keto–enol tautomerism) there are little-studied relationships and phenomena, in particular the tautomerism of phenolic compounds. These transformations aroused the interest of research workers at an early date, but the systematic study of this interesting phenomenon was made possible only by the development of modern physical methods for studying organic compounds.

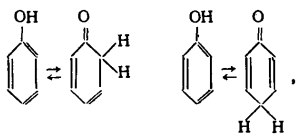
In keto–enol tautomeric transformations of organic compounds, the tautomerism of hydroxyaromatic compounds occupies a special place, since the phenomenon is accompanied by breakdown of the aromatic bond system. The present paper summarises results concerning the actual phenomenon of tautomerism in the phenol series, and also some reactions of substituted phenols (for example, salt formation), as a result of which equilibrium is established between the aromatic (phenolic) and quinonoid or quinolide†

† We apply the term "quinolide", as distinct from "quinonoid" in the description of bond systems, to cyclohexadienones in which the carbon atom in the *ortho*- or *para*-position relative to the carbonyl group is joined by ordinary (not double) bonds to two substituents.

(cyclohexadienone) bond systems. This review does not deal with the reactions of phenols in which substances with a quinolide structure are obtained merely as intermediates or are formed irreversibly by the action of electrophilic and radical reagents on substituted phenols. Reactions of the last type (phenol–dienone bond rearrangement) were reviewed in detail earlier[2]. Since we shall restrict ourselves to the regular features of equilibrium transformations in the phenol series, we shall naturally not consider processes associated with the phenomenon of mesomerism in phenolic compounds, since this is of independent interest.

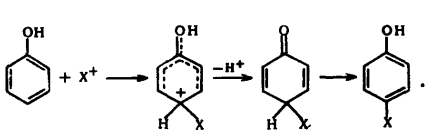
2. TAUTOMERISM OF PHENOLS

The possibility of tautomeric transformation of phenols into compounds with an *ortho*- or *para*-quinolide bond system (cyclohexadienones)



(I) (II)

is usually regarded[3,4] as a specific case of keto–enol tautomerism. Support for this view is provided by certain features which the phenomena have in common. A phenol molecule containing a hydroxyl group and a bond of aromatic type (with electron content very close to that of a double bond) should be converted into an alicyclic carbonyl compound. In reality, however, this does not take place in the simplest phenols, since the equilibrium is displaced completely towards the phenolic (enol) form. This is in fact the chief characteristic of the phenol ⇌ cyclohexadienone tautomerism which we are considering. Moreover, if it is assumed that the conversion of phenol into the cyclohexadienone with the *para*-quinolide structure (II) is energetically more favourable, phenol–dienone tautomerism, unlike keto–enol tautomerism, will not have the characteristic of a triad tautomeric transformation. Thus its mechanism should differ slightly from that of ordinary keto–enol tautomerism. Unfortunately, the question of the mechanism of phenol–dienone tautomerism remains open. Its mechanism should apparently be close to that of electrophilic substitution, which in the phenol series has characteristic features[5] associated with the intermediate formation of dienone systems of types (I) or (II). According to the mechanism at present accepted for electrophilic substitution in the phenol series (see for example Nenitzescu[6]) the first stage in the substitution is the formation of the benzonium ion (III), which is readily stabilised by the removal of a proton from the hydroxyl group with the formation of an intermediate neutral quinolide compound (IV), which rapidly isomerises into a substituted phenol. Thus for most monohydric phenols the formation of cyclohexadienone structures is possible only at the moment of reaction under the influence of an electrophilic reagent‡:

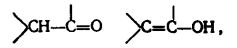


(III) (IV)

‡ See the earlier review[2] for more details.

Obviously, if it is assumed that X = H, we shall be dealing with the typical keto–enol tautomerism of phenol itself. Analogous considerations can be applied to the *ortho*-quinolide tautomer. In these transformations, however, the exact mechanism of the transformation of the dienone (IV) into the phenol has not been studied; this is directly related to the tautomerism of phenols. The question of the mechanism of phenol–dienone tautomerism is of considerable practical importance, since examples[7-9] have been described (without reference to mechanism) of the irreversible transformation of certain *para*-quinolide compounds of type (IV) into the corresponding phenols§. Moreover, even where phenol–dienone tautomerism is possible (for example, anthrol ⇌ anthrone) almost no discussion of the mechanism of these transformations has been published.

Thus all the characteristic features of phenol–dienone tautomerism are related to the extreme stability of the phenolic (enol) form. This stability is extremely regular, despite the fact that comparison of the two bond systems



shows that the formation of the carbonyl group is energetically much more favourable (by 18.6 kcal mole^{-1})[11] than that of the enol group. The possibility of partial enolisation arises, however, even in acetoacetic ester, chiefly as a result of the gain in the energy of delocalisation with another carbonyl group. In the phenol–cyclohexadienone system which we are considering, however, the gain in resonance energy (the energy of aromatic delocalisation, which for benzene amounts to ~ 36 kcal mole^{-1}[12,13]) is much greater than the energy required for enolisation of the carbonyl group, so that the aromatic bond system becomes the most favoured. Thus the simplest phenols exist in only one form and there is no possibility of tautomerism in these compounds. This conclusion is confirmed by all the chemical and physical properties of the simplest phenols. It thus becomes evident that the manifestation of phenol–dienone tautomerism is possible only when there are additional factors leading in some way to a decrease in the difference between the energies of enolisation and aromatic conjugation. The most important such factors are the following.

1. Increase in the number of hydroxyl groups in the aromatic nucleus. Here tautomerism is possible because the energy of aromatic delocalisation must compensate the energy of enolisation of not one but several carbonyl groups.

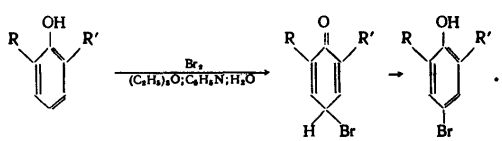
2. Formation of phenoxide ions. In the equilibrium transformation involving a phenoxide anion there is no need to expend energy on the removal of a proton, and this naturally makes the equilibrium system more labile. Moreover, the fact that the aromatic ring is always involved in the redistribution of the negative charge in the phenoxide ion should facilitate to a considerable extent the production of the carbonyl form.

§ Recently, de la Mare in a private communication[10] suggested that under the conditions of acid or base catalysis the transformation of the dienone (IV) into the substituted phenol involves initially the attachment of a proton from the solvent to the carbonyl oxygen of the dienone, followed by the removal of a proton from the *gem*-position. The mechanism may be different, however, in a spontaneous transformation.

3. Decrease in the energy of aromatic delocalisation in the phenol ring as a result of its condensation with other aromatic systems.

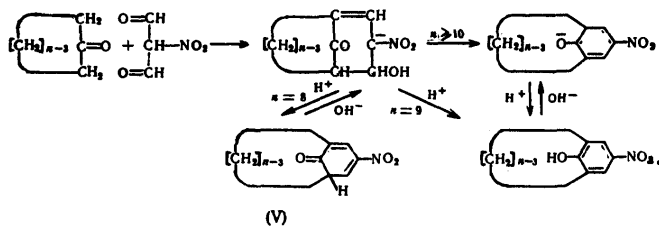
4. The introduction, into the *ortho*- or *para*-position of the phenol, of groups exhibiting a marked negative conjugation effect. Here a decrease in the energy of aromatic delocalisation takes place as a result of conjugation of the ring with the group under consideration; this may lead to a redistribution of the electron density in the molecule with the formation of a quinonoid (but not quinolide) bond system. This leads to the possibility of a slightly different tautomeric transformation of the phenol molecule, in which an electronegative group takes part in the transfer of a proton from the phenolic hydroxyl (for example, the tautomerism of nitrosophenols).

Tautomerism in phenolic compounds arises most readily when a phenolic aromatic ring is influenced simultaneously by several of the above factors. Here, the tautomerism conditions (influence of temperature and the medium) and steric phenomena are naturally of considerable importance. In the tautomerism of phenols the spatial factor (as in classical keto–enol tautomerism [14]) leads to an increase in the stability of the keto-form and retards its rearrangement into the phenol. A similar influence is shown to some extent by the steric factor even in mononuclear polyhydric phenols. For example, in the bromination of 2,6-dialkylphenols in the presence of substances exhibiting proton-accepting properties, bromo-*p*-quinolide compounds were isolated in the individual state; these isomerised spontaneously into the corresponding *p*-bromophenols [7,8]:



The lifetime of these quinolide compounds depends to a significant extent on the steric hindrance around the carbonyl group, and at 20° amounts to ten days for R = R′ = $= C(CH_3)_3$, or 4 h for R = R′ = $CH(CH_3)_2$; for R = R′ = CH_3 the bromoquinolide compounds exist only in dilute solutions and isomerise instantly into the bromophenol when attempts are made to isolate them. Stabilisation of a cyclohexadienone structure as a result of screening of the carbonyl group by t-butyl groups was also described by Kharasch [9], who by the recombination of 2,6-di-t-butylphenoxyl radicals obtained a bis-*p*-quinolide compound which readily isomerised into 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxybiphenyl.

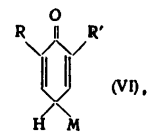
Prelog [15,16] described another type of steric influence on the stability of a cyclohexadienone having a hydrogen atom as one of the *gem*-substituents. By condensing cyclononanone with nitromalonic aldehyde followed by acidification of the reaction mixture, he obtained the dicyclic dienone (V), which is an isomeric keto-form of the corresponding nitrophenol. The dienone (V) is extremely stable and isomerisation into the phenol is prevented by the rigidity of the structure, which does not allow the formation of a double (or in this example aromatic) bond at the head of the dicyclic bridge, in accordance with Bredt's rule [17]. When the cyclic ketone is enlarged by one methylene group, however, the condensation product is converted into the nitrophenol on analogous treatment, and with further increase in the dimensions of the ring the anion of the corresponding phenol is obtained immediately in the reaction mixture:



(V)

While dealing with stabilisation of the carbonyl form by the steric factor, we should point out that for a prolonged period one could find in the literature the unrefuted opinion, put forward in 1911 by Mayer [18], that tautomerism was possible in 3,4-di-t-butylphenol because of the marked steric hindrance in the *o*-di-t-butylbenzene system [19]. This phenol was prepared in 1964, however, and it was shown to exist only in the usual phenolic form [20].

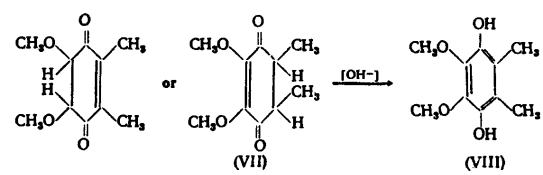
The influence of the steric effect is also seen in the formation of salts by phenols showing steric hindrance¶; some authors [21,22] on the basis of the chemical properties, have assigned the quinolide structure (VI) to these compounds in the solid state. In solution, these metal derivatives have been assigned [23,24] the structure of a levelled (ambident) ion. Treatment of these solutions with alkyl halides leads to the attachment of the alkyl residue to the phenol in the *para*-position. The quantity of C-isomer depends on the steric hindrance created by the *ortho*-alkyl groups and the magnitude of the entering alkyl group:



(VI),

where M = K, Na, or Li. Analogous reactions with these salts are undergone by benzoyl chloride [25], acrylonitrile [22,25], ethylene oxide [21], and a number of other compounds [21].

As already noted, increase in the number of hydroxyl groups in the aromatic nucleus, as a result of a decrease in the difference between the stabilisation energies of the keto- and enol forms [26], should favour tautomerism and this should be reflected in the properties and reactivity of polyhydric phenols. The individual existence of the keto-form should then be possible even when the influence of the steric effect is smaller. For example, the antibiotic gliorosein (VII), according to chemical and spectroscopic data, is an isomeric keto-form of the corresponding substituted hydroquinone (VIII), into which it can be readily converted in the presence of basic substances [27]:

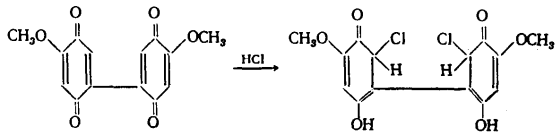


(VII) (VIII)

The formation of a similar diketo-form was also observed in the addition of hydrogen bromide to 2,6-dimethoxyquinone [28]. An analogous ketone (IX) was also obtained [29,30] in

¶ In 2,6-di-t-alkylphenols the screening of the phenolic hydroxyl is so great that these phenols do not dissolve in alcoholic solutions of alkalis and do not form salts under ordinary conditions. Salts of these phenols can be formed only by treating them with alkali metals in benzene or liquid ammonia.

the biphenyl series by the addition of hydrogen chloride to the diquinone (X). This ketone could not be enolised, however, since on recrystallisation it decomposes to the original components:



(X) (IX)

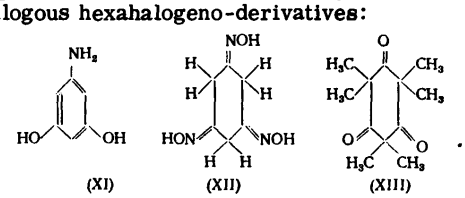
Here we see a general property of the keto-forms of substituted hydroquinones, whose stabilisation into quinonoid compounds with the removal of a molecule of an inorganic substance takes place more readily than the transformation into isomeric hydroquinones. This characteristic has been most extensively studied for compounds of the naphthalene series (see p. 823).

A large amount of material on the chemical properties and reactivity of polyhydric phenols indicates the possibility that many of these compounds react in a tautomeric keto-form. Thus resorcinol, like $\alpha\beta$-dicarbonyl compounds, is readily reduced by sodium amalgam to cyclohexane-1,3-dione[31].

The behaviour of phenols, containing different numbers of hydroxyl groups, in their reactions with ammonia is also characteristic. The replacement of the phenolic hydroxyl group in a monohydric phenol by an amino-group takes place with difficulty and under very severe conditions (350–450°, 50–60 atm), whereas with resorcinol this reaction takes place fairly readily at ~ 200°,[32] and phloroglucinol is converted almost quantitatively into 5-aminoresorcinol (XI) at room temperature in alcoholic ammonia solution[33,34]. These reactions evidently take place by the same mechanism as the action of ammonia on carbonyl compounds capable of undergoing prototropic transformations[35].

Finally, the reaction of phloroglucinol with hydroxylamine is extremely specific. As early as 1886, Bayer[36], in a study of this reaction, isolated a compound to which he assigned the structure of the cyclic trioxime (XII). Much later (1956) the structure of this substance was confirmed by spectroscopic methods[37]. Its infrared spectra show bands corresponding to the absorption of the –C=N group (1653 cm^{-1}), and the ultraviolet spectrum does not contain the maximum due to aromatic absorption.

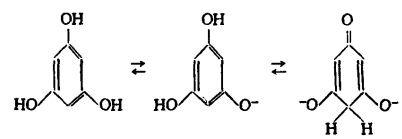
Unusual behaviour is shown by phloroglucinol and resorcinol[38-45] on alkylation by alkyl halides in aqueous alkali. Thus methylation by methyl iodide in the presence of potassium hydroxide gives a mixture of *O*- and *C*-methyl derivatives, and with an excess of methyl iodide the hexamethyl derivative (XIII) can be obtained from phloroglucinol[40-44,46-48]. A more detailed study[49] of this reaction for the example of 2,4,6-trihydroxyacetophenone showed that the composition of the mixture of final products depends to a marked extent on the concentration of alkali in the solution. This reaction resembles the alkylation of metallic derivatives of acetoacetic ester. Chlorination[50,51] and bromination[52,53] of phloroglucinol with an excess of halogenating agent also gives analogous hexahalogeno-derivatives:



(XI) (XII) (XIII)

On the other hand, there are reactions in which phloroglucinol behaves as a typical phenol: it gives the triacetate with acetyl chloride, and it is methylated by diazomethane with the formation of the trimethyl ether[54,55].

Thus the chemical properties of polyhydric phenols, in particular phloroglucinol, indicate that the compounds may react in both the keto- and enol forms. Tautomerism in phloroglucinol has not been observed directly, however. The Raman[56], ultraviolet, and infrared[37] spectra indicate that phloroglucinol consists exclusively of trihydroxybenzene both in solution and in the solid state. Naturally, here it might be assumed that phloroglucinol contains in equilibrium extremely small quantities of the keto-form, which are not detected by the methods used. It is more probable, however, that the dual reactivity of phloroglucinol is due to the tautomeric transformation of its anion, since all the reactions confirming the existence of the keto-form of phloroglucinol generally take place in the presence of bases. The existence of the phloroglucinyl oxide anion in the tautomeric keto-form can now be taken as proved, so that the question of the tautomerism of phloroglucinol reduces to the tautomerism of its anion; the most stable keto-form should be the doubly-charged phloroglucinyl oxide anion:



According to a number of authors[57-61], evidence for this is provided by the appearance of a maximum in the 250 nm region, characteristic of *para*-quinolide compounds, in the ultraviolet spectrum of an alkaline solution of phloroglucinol. Formation of this structure is also indicated by the sharp increase in the second dissociation constant of phloroglucinol compared with other polyhydric phenols (Table 1).

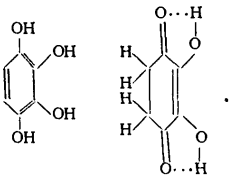
Finally, the existence of the doubly-charged phloroglucinyl oxide anion in the keto-form was proved most convincingly by proton magnetic resonance[63]. The PMR spectrum of aqueous phloroglucinol solution shows a single maximum corresponding to aromatic protons (τ = 3.95), which is displaced slightly when one mole of alkali is added (τ = 3.98). The addition of a second mole, however, produces sharp changes in the spectrum: the maximum due to the aromatic protons disappears, with the production of two new peaks; one of these (τ = 4.97) corresponds to protons associated with an alkene double bond, and the other (τ = = 7.00) corresponds to the protons of a methylene group. The chemical shift of the observed peaks is insensitive to change in concentration and temperature. These observations indicate the existence of a doubly-charged anion in the form of an alicyclic isomer, and according to the infrared

TABLE 1. Dissociation constants of polyhydroxyphenols[62]

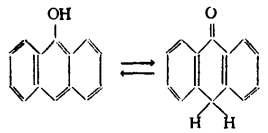
Phenol	$10^9 K_1$	$10^{12} K_2$
Phloroglucinol	3.56	1320.00
Pyrogallol	9.67	2.30
Resorcinol	0.71	4.78
Pyrocatechol	0.75	0.84
Hydroquinone	0.12	0.91

spectra[63] this structure is preserved in the disodium salt of phloroglucinol in the solid state. It thus follows that un-ionised phloroglucinol and singly-charged and doubly--charged ionic forms are present in equilibrium, and pure tautomerism between two forms of the doubly-charged anion is not observed. The formation of the doubly-charged phloroglucinyl oxide anion is apparently accompanied by simultaneous rearrangement of the aromatic bond system into a dienone system; this is extremely characteristic of the ionisation of certain substituted phenols (see p. 828).

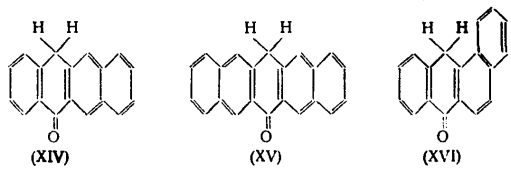
As a result of the introduction of another hydroxyl group into the aromatic ring, 1,2,3,4-tetrahydroxybenzene can exist in two individual isomeric forms[64,65]. Under appropriate conditions the isomers can be converted into one another, but there is no reversible equilibrium between them. Here the stability of the keto-form is influenced not only by the above energetic features, but also by intramolecular hydrogen bonds formed as a result of the favourable mutual arrangement of the hydroxyl and keto-groups (see p. 822).



The above published data indicate that in the mononuclear phenol series (mono-, di-, and poly-hydric), actual tautomerism, as a mobile equilibrium, does not exist. This state of affairs is not preserved, however, on going to the hydroxyl derivatives of polycondensed aromatic systems. Even in naphthols the symmetrical character of the π-electron cloud is disturbed, and this naturally leads to a decrease in the aromaticity of the phenolic ring. Approximate quantum-mechanical calculation shows that the 1–2 bonds of naphthalene are closer to double bonds than the bonds in benzene, and also that the 1,2,3,4-system of naphthalene is similar to some extent to the buta-1,3-diene system and to an even greater extent to the 1,4-diphenylbuta--1,3-diene system[66]. Thus the energy used in enolisation is compensated to a smaller extent by the energy of aromatic delocalisation in the naphthol series than in mononuclear hydroxyaromatic compounds. As a result, in the naphthalene series, even the monohydric hydroxyl derivatives exhibit the properties of the tautomeric keto-form in their chemical reactions. Thus β-naphthol is readily reduced to β-tetralone[67,68], undergoes bromination with the formation of derivatives of the keto-form with *gem*-substituents in the α-position[69], etc. As in phloroglucinol, however, tautomerism is not observed directly in the naphthols. In monohydric phenols tautomerism becomes possible only when the phenol ring is condensed with two aromatic nuclei. Thus in unsubstituted anthracene the energy of aromatic delocalisation is slightly greater than the sum of the energy of conjugation of two isolated aromatic rings[70], but when a hydroxyl group is introduced into the *meso*-position of anthracene, this excess delocalisation energy cannot completely compensate the enolisation energy. As a result, 9-hydroxyanthracene (anthrol) is able to undergo reversible conversion into the corresponding ketone (anthrone) in which the two isolated aromatic rings are conjugated with the carbonyl group, leading to an even greater increase in the stability of the keto-form:



Thus the appearance of tautomerism in a phenolic compound indicates a decrease in the aromaticity of the ring attached to the hydroxyl group. This is readily seen on going from phenol to other monohydroxy-derivatives of polycondensed aromatic compounds. The more extensive the polynuclear aromatic system, the greater the probability of conversion of the enol form into the keto-form, and the greater the stability of the keto-form. Thus the keto-form of hydroxynaphthacene (XIV) shows only a slight tendency to undergo enolisation, and the phenolic form of the pentacenes (XV) is unknown[4]:

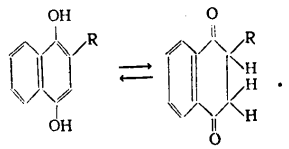


An attempt to bring about the isomerisation of (XV) in the usual way by heating in concentrated sodium hydroxide was unsuccessful. The isomer of hydroxynaphthacene — benzanthrol (XVI) — however, exists in both forms, which can be readily separated[71].

Of the above possible tautomeric transformations, the tautomerism of anthrol has been most studied. This is at present perhaps the simplest monohydroxyaromatic compound for which two isomeric forms are known to exist in equilibrium. As early as 1911, Mayer[18] found that the anthrol–anthrone equilibrium can exist in the absence of catalysts. A more detailed study[72] showed that in alcohol, 9-anthrone is enolised to the extent of only 11.5%. Slow cooling leads to crystallisation of the non-enolised product, but on rapid cooling the mixture contains crystals of 9-anthrol. The two forms are distinguished by their chemical properties. The keto-form shows a relatively low activity in the absence of catalysts bringing about enolisation. Heating in 10% sodium hydroxide for 10 min in a current of nitrogen with subsequent acidification leads to complete enolisation of anthrone. The reverse isomerisation takes place, however, when the resulting 9-anthrol is dissolved in ether, alcohol, or dioxan[73]. Alkylation of 9-anthrone by benzyl chloride in the presence of alkali gives 10,10-dibenzyl-9-anthrone. Hydrolysis of 9-benzyl--10-benzyloxyanthracene by treatment with hydrochloric acid leads to rapid isomerisation of the resulting 10-benzyl--9-anthrol into the corresponding anthrone[74]. Kinetic studies of the isomerisation of anthrol into anthrone showed that this reaction is of first order, the activation energy and rate of isomerisation depending to a marked extent on the solvent[75].

On going to polyhydroxy-derivatives of condensed hydrocarbons, all the above features are shown even more clearly, and the possibility of tautomeric transformations arises in dihydroxynaphthalenes containing both hydroxyl groups in the same ring, particularly if on formation of the keto-form the carbonyl groups are further stabilised by conjugation with the other aromatic ring. These changes were studied in

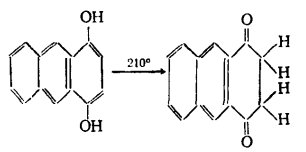
most detail by Thomson[4,76-80]. 1,4-Dihydroxynaphthalene (R = H) and 1,4-dihydroxy-2-methylnaphthalene (R = CH_3) on fusion (~ 200°) form equilibrium mixtures containing 10% of the diketo-forms (XVIII):[76,81,82]



(XVII) (XVIII)

Under ordinary conditions, however, both the dienol (XVII) and the diketone (XVIII) are stable compounds, and equilibrium between them does not exist. According to Braude's data[83], in the titration of the hydroquinone (XVII) with cerium sulphate in petroleum ether solution at 130°, the titre decreases gradually to a definite limit. Tautomeric equilibrium is evidently established under these conditions also. The reverse conversion of the diketone (XVIII) into the dienol (XVII) takes place when the diketone is dissolved in cold alkali and the resulting solution is acidified. Spectroscopic studies[76] showed that under ordinary conditions the diketone (XVIII) undergoes no structural changes in solution or in the solid state.

In the anthracene series the ability of 1,4-dihydroxy--derivatives to undergo conversion into the diketo-form is even greater, and this is naturally associated with a further decrease in the aromaticity of the phenolic ring. Thus on fusion (210°) 1,4-dihydroxyanthracene (XX) is converted in 50% yield into the corresponding 1,2,3,4-tetrahydro-1,4--diketoanthracene (XIX):[78]

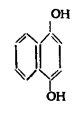
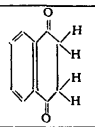
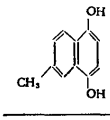
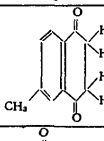
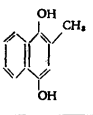
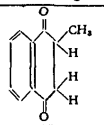
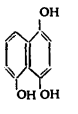
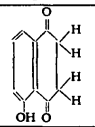
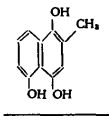
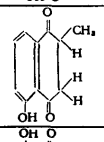
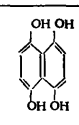
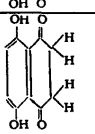


(XX) (XIX)

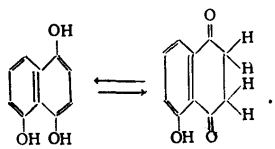
Here the diketone is more stable than the dienol. The diketone can be converted into the dienol by dissolving in dilute alkali. Analogous properties are shown by 1,4-dihydroxy-9,10-diphenylanthracene[84]. The equilibrium 9,10-dihydroxyanthracene–anthraquinol system is also well known[85].

The stability of the diketo-forms of the 1,4-dihydroxy--derivatives of polycondensed compounds which we have considered increases appreciably when hydroxyl groups are introduced into the α-position of a neighbouring aromatic ring. This increased stability is due to the production of an intramolecular hydrogen bond in the keto-form as a result of the favourable spatial arrangement of the hydroxyl and carbonyl groups. In these compounds, the energy of aromatic delocalisation compensates not only the energy of enolisation of the two carbonyl groups, but also the additional energy of rupture of the hydrogen bond, and this should naturally decrease the stability of the enol form and displace the equilibrium (relative to the 1,4-dihydroxy-derivatives) towards the diketone[78,86] (see Table 2). The representatives of this series which have been most studied

TABLE 2. Influence of the number of hydroxyl groups on tautomeric equilibrium in the naphthol series.

Formula of phenol	Keto-form	Conditions of tautomeric equilibrium	Composition of tautomeric mixture (% keto-form)	Refs.
	exists only as the phenol, but in a number of reactions exhibits the properties of the keto-form			78
		in the molten state; 200–210°	10.5	76
		in the molten state; 190–200°	17	78
		in the molten state; 200–210°	11	76
		1. in the molten state; 200–210° 2. boiling in acidic aqueous solution	67 19	76
		in the molten state; 200–210°	41	77
		exists almost entirely in the keto-form		76

are 1,2,5-trihydroxynaphthalene (α-hydrojuglone) and its 2-methyl homologue[76,77] †:



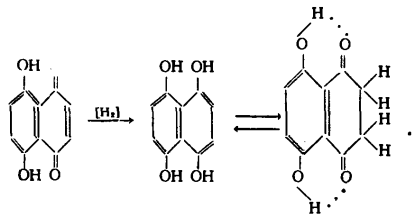
(XXI) (XXII)

The isomers (XXI) and (XXII) may exist in the equilibrium state in aqueous solution. The structures of both substances have been confirmed by spectroscopic data[76,87].

These regular features are shown even more clearly by 1,4,5,8-tetrahydroxynaphthalene, for which the conversion into the keto-form is accompanied by the production of two intramolecular hydrogen bonds. Accordingly, its keto--form (β-hydronaphthazarin) becomes more stable and this is naturally reflected in the properties of this compound.

† The diketone (XXII) — β-hydrojuglone — is present as glucosides in walnut extracts. Under the conditions of its extraction (boiling aqueous solution) it is partly converted into the enol--form — α-hydrojuglone[76].

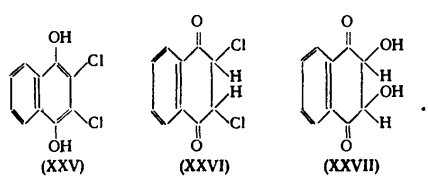
Thus 1,4,5,8-tetrahydroxynaphthalene (α-hydronaphthazarin) (XXIII), formed by the reduction of naphthazarin, is converted almost quantitatively under the conditions of the reaction into the isomeric β-hydronaphthazarin (XXIV):[88]



(XXIII) (XXIV)

The diketo-structure of β-hydronaphthazarin was proved by chemical methods[76,88]. Analogous behaviour is shown by the product of the reduction of quinizarin — leuco-quinizarin (1,2,3,4-tetrahydro-9,10-dihydroxy-1,4-diketoanthracene)[86,89]. The influence of the number of hydroxyl groups on tautomerism in the hydroxynaphthalene series is illustrated in Table 2.

A unique place in the 1,4-dihydroxynaphthalene series is occupied by compounds containing substituents (Hal, OH, SH, SO_3Na, etc.) capable of being removed. Here there are no reversible tautomeric transformations between the isomers, despite the fact that these compounds may exist in the individual state in both keto- and phenolic forms. These phenols are not converted into the diketones on fusion, since they usually decompose at elevated temperatures. On the other hand, the keto-forms, instead of enolising, are more readily converted into a quinonoid system with the removal of a molecule of an inorganic substance. Typical representatives of this type of compound are the isomeric 2,3-dichloro-1,4-dihydroxynaphthalene (XXV) and the dichlorodihydronaphthoquinone (XXVI). The latter readily loses a molecule of hydrogen chloride and is converted into 2-chloro-1,4-naphthoquinone[79].

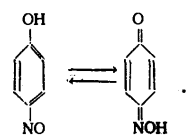


(XXV) (XXVI) (XXVII)

The keto-forms of these dihydroxynaphthalenes are in turn often obtained as a result of 1,2-addition to naphthoquinones[90-92]. Certain substituted diketones of the naphthalene series are nevertheless able to undergo irreversible enolisation — for example, (XVII) — but in these instances the reaction in this direction always competes with that involving elimination[93]. The individual properties of these compounds have been examined by Thomson[4].

3. TAUTOMERISM OF NITROSOPHENOLS

The introduction of electronegative substituents into the *ortho*- and *para*-positions of a phenol brings about a redistribution of the electron density in the molecule, leading to a decrease in the energy of aromatic conjugation and appreciable polarisation of the hydrogen–oxygen bond in the hydroxyl group. This facilitates the removal of hydrogen as a proton and leads to the appearance of keto–enol tautomerism. These features should be shown to the greatest extent in the nitrosophenol molecule, since the nitroso-group exhibits the greatest negative conjugation effect. Moreover, a distinguishing characteristic of the nitroso-group is its ability to combine with a proton using the unshared pair of electrons of the oxygen atom, with the formation of a hydroxyimino-group; this in turn should lead to additional stabilisation of the carbonyl form of the nitrosophenol as a result of the formation of a quinonoid system of conjugated bonds. Thus in the example which we are considering, there is on the one hand a decrease in the energy of aromatic conjugation in the phenolic form as a result of the presence of the nitroso-group and on the other hand an increase in the energy of enolisation of the carbonyl group, which is further stabilised by quinonoid conjugation. The final result of these two factors, operating in the same direction, is that in the nitrosophenol series the benzenoid (phenolic) form is less favoured than its isomeric quinone oxime form. Calculations by Jaffe[94] using the molecular orbital method showed that for 4-nitrosophenol the quinonoid state is favoured relative to the phenolic form to the extent of 4.6 kcal mole^{-1}. Experimental data published up to the present confirm that nitrosophenols exist chiefly in the quinonoid form. As a result, nitrosophenol $\rightleftharpoons$ quinone oxime tautomerism exhibits certain characteristic features compared with phenol–dienone tautomerism, particularly the marked sensitivity of the equilibrium to the medium, and the specific influence of substituents in the benzene ring:



Since in *o*-nitrosophenols an intramolecular hydrogen bond is formed, inevitably producing an additional influence on the characteristic features of the tautomeric equilibrium, we shall consider first the tautomerism of *p*-nitrosophenols.

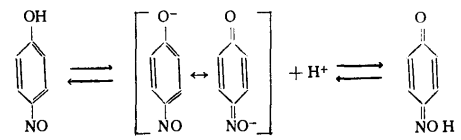
Facts indicating the tautomeric properties of *p*-nitrosophenol have been known for a long time. Bayer[95] as early as 1874, and later Goldsmidt[96], found that *p*-benzoquinone monoxime, formed by the reaction of *p*-benzoquinone with hydroxylamine, is identical in all respects to *p*-nitrosophenol obtained by the direct nitrosylation of phenol. It was found that in oxidation and reduction this compound behaves as a nitroso-compound, whereas on treatment with hydroxylamine it gives the quinone dioxime, that is, it reacts in the quinonoid form.

These data indicated the possibility of the reversible interconversion of *p*-nitrosophenol and *p*-benzoquinone monoxime. The first attempts to investigate the regular features of this transformation were undertaken using chemical methods[97-105] but no definite conclusions could be reached. The results obtained merely indicated the existence of a tautomeric equilibrium between the phenolic and

quinonoid forms. Thus it was shown that the phenolic form of nitrosophenols is converted into the quinonoid form by heating in the presence of acids [100,105] or by acidifying their alkaline solutions [106]. The two isomeric forms of the nitrosophenols give identical silver salts, which on treatment with methyl iodide give the methyl ethers of the benzoquinone oximes [102]. An analogous product is formed by the reaction of nitrosophenols with methyl sulphate in alkaline medium [102]. On the other hand, an attempt, using *p*-nitrophenylhydrazine, to determine the concentration of the quinonoid isomer in the products of the nitrosylation of phenol was unsuccessful, since all the nitrosophenol was converted into the corresponding *p*-nitrophenylhydrazone [102]. The reaction with diazomethane was found to be more suitable; diazomethane reacts with nitrosophenol in ether solution to give two products: glyoxime *NN'*-di-4-methoxyphenyl ether and benzoquinone 4-oxime *O*-methyl ether [104]. The results obtained could not be used, however, to determine the ratio of the tautomeric forms of the nitrosophenol. By 1930–1932 the opinion had been formed, on the basis of the above properties, that nitrosophenols exist chiefly in the phenolic form in the crystalline state and in inert solvents. Thus chemical methods proved unsuitable for the determination of the composition of tautomeric mixtures of nitrosophenols. The solution of these problems was made possible only by the application of spectroscopic methods, which without disturbing the equilibrium in the system, allowed its qualitative composition to be determined unambiguously and some information on its quantitative composition to be given.

The absorption spectrum of the products of the nitrosylation of phenols was first obtained by Hartley [107]. By comparing the spectrum of the products of the nitrosylation of phenol with the spectrum of *p*-nitrosoaniline, he established that the chief component of the mixture in ether solution is the quinonoid form. Baly [108], who repeated these studies, however, put forward the opposite opinion. This problem was later studied by Anderson [109]. By studying the absorption spectra of *p*-nitrosophenol in ether solution and comparing the results obtained with the spectra of the methyl ethers of the two isomeric forms of *p*-nitrosophenol, he showed that under these conditions the equilibrium mixture consists of approximately 70% quinone oxime and 30% nitrosophenol. Analogous results were obtained for solutions of nitrosophenol in dioxan, chloroform, and absolute alcohol. The most recent studies [110] of the infrared spectra of dilute solutions of *p*-nitrosophenol in carbon tetrachloride confirmed these data. When ultraviolet spectroscopy was applied to the study of the tautomerism of 2- and 3-substituted nitrosophenols, determination of the position of the maximum characteristic of the pure nitroso-form was found to be very difficult, since the equilibrium is generally displaced towards the quinonoid form and the more intense band due to the latter masks the band due to the nitroso--form. In this connection, the correctness of the interpretation of spectroscopic data in the determination of the characteristic features of the tautomerism of substituted nitrosophenols has been discussed [99,109,111,112].

The further development of spectroscopic methods has made it possible to return to this question and to solve the problem of determining the changes in the absorption spectra of the phenolic and quinonoid forms of nitrosophenols, irrespective of the number and nature of substituents [113]. In particular, detailed study of the spectroscopic properties of the products of the nitrosylation of phenol led a group of French workers [113-117] to recognise the existence of a three--component mixture in the tautomerism of nitrosophenols: the nitrosophenol, the quinone oxime, and an intermediate ionised form — the ambident ion‡:



Thus in the tautomerism of nitrosophenols, as in keto–enol tautomerism [1], the two forms first give up a proton with the formation of the same anion in each instance.

The use of spectroscopic methods has made it possible to establish the dependence of the equilibrium in a nitrosophenol–quinone oxime system on the nature of the solvent, the pH of the medium, and the position and nature of the substituents. In an aqueous medium, the above system of reversible transformations is considerably simplified and usually consists of two components. Moreover, under these conditions the tautomeric systems are extremely sensitive to changes in the pH of the medium only in the range from 3 to 7, and are independent of pH outside this range [112]. This phenomenon is associated with the ionisation of the two tautomers. In a strongly acidic medium (pH < 3), the ionisation should be suppressed, leading to a displacement of the equilibrium in one direction and the existence of only one neutral form, exhibiting the lowest acidity. In a strongly acidic medium this will in fact be the quinone oxime form. Similarly, in an alkaline medium (pH > 7) the un-ionised forms do not exist and in accordance with the total ionisation the intensity of the absorption becomes almost constant [112].

In a study of the ultraviolet spectra of aqueous solutions of unsubstituted *p*-nitrosophenol, the presence of two components (ionic and quinone oxime forms) in the system was confirmed by the existence of an isosbestic point [119]. These spectra were also used to calculate the dissociation constant of the oxime form ($pK = 6.21 \pm 0.03$); this quantity was also determined by conductimetric and potentiometric titration [119].

In neutral solvents, nitrosophenols exist in all three equilibrium forms, the quantity of ionic form increasing sharply with increase in the polarity of the solvent (ether, alcohol, water). The quantity of nitroso-form decreases and the proportion of oxime form increases in the same order [115].

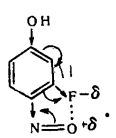
The introduction of alkyl substituents in the 2-position of the aromatic nucleus also increases the displacement of the entire system towards the quinonoid form. Thus in alcoholic solution, *p*-nitrosophenol and 3-methyl-4-nitrosophenol give maxima corresponding to all three forms (nitrosophenol, oxime, and ionic) with the oxime form predominating, whereas the introduction of alkyl substituents in the

‡ The *p*-nitrosophenol–quinone oxime tautomeric mixture was recently analysed by paper chromatography [118]. On the basis of the agreement between the calculated and experimental R_M values $\left(R_M = \log\left[\frac{1}{R_F} - 1\right]\right)$, it was assumed that the tautomeric mixture consists chiefly of nitrosophenol together with a small percentage of the oxime. No allowance was made, however, for the existence of the anionic form or for the exceptionally marked dependence of this equilibrium on the nature of the medium.

2-position leads to the disappearance or sharp decrease in the quantity of the nitroso-form in the equilibrium system [115]. Increase in the steric hindrance at the hydroxyl group, created by branched alkyl substituents, produces a completely quinonoid system — alcoholic solutions of these compounds contain only the oxime form [115]. This relationship has been studied in most detail by Finch [120] for 2,6-dialkylnitrosophenols where Alk = CH_3, C_2H_5, $CH(CH_3)_2$, or $C(CH_3)_3$. The opposite relationship is observed when the alkyl substituents are introduced into the 3,5-positions of the nitrosophenol. In this instance there is an increase in the proportion of the phenolic form in the tautomeric equilibrium in the order Alk = CH_3, C_2H_5, $CH(CH_3)_2$, and $C(CH_3)_3$. Branched substituents in the 3,5-positions apparently create additional steric hindrance to the conversion of the nitroso-form into the oxime form, and this naturally leads to an increase in the proportion of the benzenoid form [120].

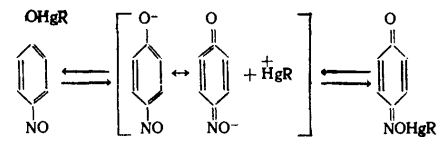
An analogous relationship is observed for the halogeno--derivatives of nitrosophenols. Thus the introduction of halogen into the 2-position of the aromatic nucleus displaces the equilibrium towards the oxime form [116]. An alcoholic solution of 2,6-dichlorobenzoquinone oxime contains only the oxime form with a small quantity of the ionised form. The same is observed for the corresponding bromo-derivatives [117]. The introduction of halogen into the 3-position, however, leads to a decrease in the proportion of the quinone oxime form in the equilibrium [115]

A unique position among halogeno-derivatives of *p*-nitrosophenols is occupied by 3-fluoro-4-nitrosophenol. This phenol cannot be converted into the isomeric 3-fluorobenzoquinone oxime. When its alkaline solution is heated and then acidified, the nitroso-form is precipitated unchanged [106]. This phenol also exists only in the nitroso--form in acidic and neutral media, irrespective of the nature of the solvent [121]. Spectroscopic studies [106] of 3-fluoro-4-nitrosophenol indicate extensive polarisation of the nitroso-group, leading to the formation of a partly bipolar structure, which by interaction of the fields may form a characteristic five-membered ring. With this bipolar structure, the oxygen atom of the nitroso-group is apparently unable to combine with a proton from the medium:



The regular features of the tautomeric equilibrium are not altered significantly on going from *p*-nitrosophenol to 4-nitrosonaphth-1-ol. With this also, the oxime form predominates in polar solvents [122], the ionic form predominates in alkaline medium [123], and the oxime form predominates in the solid state [124].

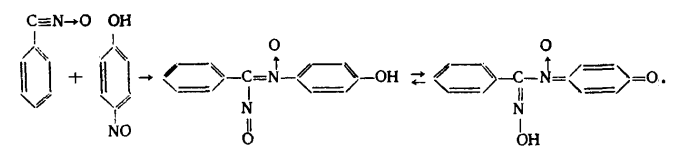
Tautomerism is also shown by the alkylmercury derivatives of *p*-nitrosophenols. In a study of the infrared spectra of these compounds, Nesmeyanov and Kravtsov [125] found that the intensity of the band due to the nitroso-group shows a definite relationship to the nature of the solvent and is independent of the concentration of substance. Since the infrared spectra indicate that in the solid state the alkylmercury derivatives of nitrosophenols have the quinone oxime structure, the observed phenomenon must be due to the existence of a tautomeric equilibrium with the intermediate formation of a common anion:



This feature is also shown by nitrosophenols with substituents in the ring, the introduction of alkyl substituents in the 2-position leading to a decrease in the concentration of the nitroso-form of the alkylmercury derivative in the solution.

An interesting feature is that interconversion of the isomers is also possible for the *O*-acetyl derivatives of nitrosophenols. For example, *O*-acetylnitrosophenol is converted quantitatively into the more stable *O*-acetylbenzoquinone oxime on recrystallisation [116].

Among other nitrosophenol derivatives, the possibility of tautomerism is observed in the products of the condensation of nitrosophenols with the oximes of certain nitriles; the 4-nitrosophenol derivative exists chiefly in the phenolic form, whereas the 1-nitrosonaphth-2-ol derivative exists in the quinonoid form [126]:

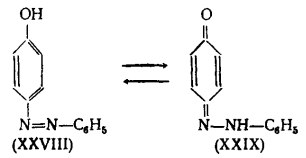


The regular features of the tautomerism of nitrosophenols are slightly different for the *ortho*-isomers. This is due to the existence [127] in these substances of an intramolecular hydrogen bond which has a fairly strong stabilising action on the nitroso-group, so that the energetic relationships between the phenolic and quinonoid (here, *ortho*--quinonoid) structures is altered slightly and the benzenoid form of the nitrosophenol is preferred. The ultraviolet spectra [127] show that *o*-nitrosophenol exists only in the phenolic form in non-polar solvents. The introduction of substituents exhibiting positive conjugation effects into the *para*-position relative to the nitroso-group, however, facilitates the rearrangement of the nitroso-group into the oxime group. Thus 2-nitroso-5-methoxyphenol and 2-nitroso--5-dimethylaminophenol [127] exist in solution in the form of tautomeric mixtures; the quinonoid form predominates, and its concentration increases with increase in the polarity of the solvent. These spectroscopic data agree with certain chemical properties. In particular, the crystallisation of 2-nitroso-5-methoxyphenol [128] from ethanol and benzene gives crystals with different appearance and melting points. These were assumed to be two tautomeric forms. With the *o*-nitrosophenols of the naphthalene series (1-nitrosonaphth-2-ol and 2-nitrosonaphth-1-ol) there is tautomeric equilibrium with the nitroso-form predominating [129].

4. TAUTOMERISM OF AZOPHENOLS

The azo-coupling of phenols, together with the data obtained by Zincke [130], who showed that hydroxyazo-compounds with analogous structure are formed by the action of arylhydrazines on the corresponding quinones, indicated the

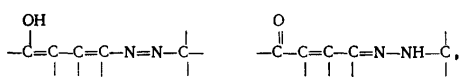
possibility of tautomeric equilibrium between azophenols and quinone arylhydrazones. A number of authors [131-138] suggested that this equilibrium is an ordinary prototropic transformation with migration of a proton between the nitrogen atom and the phenolic oxygen. This transformation is accompanied by rearrangement of the benzenoid bond system into a quinonoid system or by the opposite rearrangement of the quinonoid system into the benzenoid system:



(XXVIII) (XXIX)

The first studies of this tautomerism by chemical methods were carried out in 1929, when Borshe and coworkers [139] used dinitrophenylhydrazine to isolate the hydrazone form (XXIX) as the dihydrazone from the tautomeric mixture. The results obtained were not conclusive, since the dihydrazone can be formed directly from the monohydrazone by heating in acidic medium. Attempts to prove the existence of tautomerism in the azophenol series by chemical methods include the use of the reaction with cyclopentadiene, which according to the diene synthesis scheme gives the products of the addition to the quinonoid ring of the hydrazone form [140]. Direct confirmation of tautomerism in the azophenol series by isolation of both tautomeric forms from the equilibrium mixture has not been obtained. Only the use of spectroscopic methods made it possible to study effectively the regular features of the tautomerism of azophenols [141-152]. The successful solution of this problem was greatly assisted by the distinct separation of the spectroscopic characteristics of these tautomeric forms in the ultraviolet range.

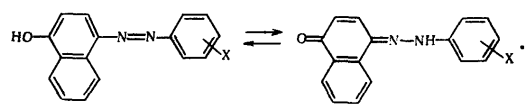
The energetic relationships for the formation of the two forms (azophenol and quinone hydrazone) facilitate tautomerism to a greater extent than in the unsubstituted phenols. Summation of the bond energies of the systems



gives 432 kcal mole^{-1} for the enol-form and 456 kcal mole^{-1} for the keto-form, that is, the formation of the keto-form is favoured to the extent of 24 kcal mole^{-1}. Thus the energy of enolisation of the carbonyl form (particularly with allowance for the quinonoid conjugation) of the azophenols is much greater than the energy of enolisation required in the formation of unsubstituted phenols, leading to a lower stability of the aromatic system. Hence the factors determining the appearance of tautomerism in the phenol series (see p. 818) should be shown even more clearly in the azophenols. The accumulation of aromatic rings condensed with the azophenol nucleus does in fact lead to more rapid conversion of the phenols into the isomeric quinonoid compounds. Thus in the solid state, compounds of the benzene series exist in the benzenoid form, whereas derivatives of the naphthalene and anthracene series exist only in the quinonoid form [149]. In solutions this change is more regular [150,153]. For example, 4-phenylazophenol always exists in only one form and exhibits a single absorption maximum (343 nm) corresponding to the azo-form, whereas 4-phenylazonaphth-1-ol and 4-phenylazoanthr-1-ol show maxima corresponding to the azophenol form (392 and 442 nm respectively) and the quinone hydrazone form (475 and 506 nm). Finally, 9-phenylazoanthr--10-ol shows only one maximum in the ultraviolet range, corresponding to the quinone hydrazone form [151]. Thus among the *p*-azophenols which we have considered, tautomeric equilibrium is found only in the derivatives of 4-azonaphthols and related compounds.

The influence of the nature of the substituents on the tautomerism of azophenols is also shown extremely clearly. Here, all the regular features characteristic of the tautomerism of phenolic compounds are preserved. The introduction of electron-accepting substituents into the molecule leads to an increase in the concentration of the keto-form, whereas the presence of electron-donating substituents facilitates the production of aromatic properties in the ring and displaces the equilibrium towards the phenolic structure. It should be noted that tautomerism is found only in the phenyl(or aryl)azophenols, but not in alkylazophenols. This is due to the fact that the phenylazo-group produces a greater displacement of electrons into the aromatic ring of the phenol, facilitating the removal of a proton and conversion into the carbonyl form. A similar influence is shown by the introduction of substituents into the phenyl nucleus of the hydrazone.

All the regular features of the influence of substituents on the tautomeric equilibrium have been studied for 4-azonaphth-1-ol derivatives:



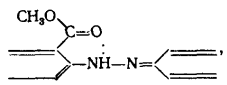
The data [154-156] in Table 3 show the influence of substituents in the phenyl ring of the hydrazone on the tautomeric azophenol ⇌ quinone hydrazone system. The ratio of the extinctions ($\epsilon_{hydrazo}/\epsilon_{azo}$) indicates approximately the proportions of the tautomers in the equilibrium mixture. Electron-donating substituents decrease this ratio, that is, they decrease the proportion of hydrazo-form, whereas electron--accepting substituents increase this ratio. A characteristic feature is that the introduction of substituents in the 2-position usually increases the proportion of the hydrazone tautomer to a much greater extent than the introduction of an analogous group in the 4-position. This anomaly is related to the possibility of intramolecular hydrogen bond formation. Thus the introduction of a carboxyl group in the 2-position [157] stabilises the hydrazone form as a result of the formation of an intramolecular hydrogen bond. Maximal stability of the keto-form, as expected, is shown by the 2,4-dinitrophenylhydrazones. Here the negative conjugation effect of the substituent in the phenol molecule

TABLE 3. Influence of substituents on the tautomerism of azonaphthols.

Substituent X	4-Arylazonaphth-1-ol $\epsilon_{hydrazo}/\epsilon_{azo}$	1-Arylazonaphth-2-ol $\epsilon_{hydrazo}/\epsilon_{azo}$	Substituent X	4-Arylazonaphth-1-ol $\epsilon_{hydrazo}/\epsilon_{azo}$	1-Arylazonaphth-2-ol $\epsilon_{hydrazo}/\epsilon_{azo}$
4'-NH_2	—	0.17	3'-OCH_3	0.89	1.41
4'-OH	—	0.40	3'-Cl	1.50	—
4'-OCH_3	0.22	0.45	3'-NO_2	1.90	2.0
4'-CH_3	0.39	1.08	2'-CH_3	0.23	1.71
H	0.63	1.31	2'-Cl	0.50	—
4'-Cl	0.84	1.26	2'-OCH_3	0.90	2.0
4'-NO_2	2.0	2.00	2'-NO_2	2.0	2.0
4'-$COOCH_3$	2.0	—	2'-$COOCH_3$	2.0	—

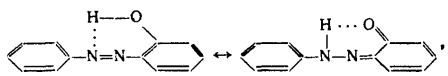
increases to such an extent that tautomerism is possible in mononuclear azophenols [140].

In the 4-phenylazonaphth-1-ol series, the NH and OH groups present in the hydrazo- and azo-tautomeric forms, are able to form hydrogen bonds with the solvent. Since these bonds have different strengths, the tautomers may be stabilised by these bonds to different extents. Moreover, substituents in the 2-position of the benzene ring will also influence the strength of the hydrogen bonding with the solvent, either by the formation of intramolecular hydrogen bonds of the type



or by creating steric hindrance to the formation of an intermolecular hydrogen bond. The influence of solvents on the tautomeric equilibrium has also been studied [148] for 4-phenylazonaphth-1-ols. For the 3′- and 4′-substituted compounds the concentration of the hydrazone tautomer increases with increase in the polarity of the solvent in the order: hexane < benzene < chloroform < 50% ethanol < < CH_3COOH. The picture is complicated considerably in the presence of 2-substituents capable of forming intramolecular hydrogen bonds (Cl, OCH_3, etc.). The proportion of hydrazo-form is smaller in polar solvents (water, ethanol, CH_3COOH) than in hexane, benzene, and chloroform. An explanation for this anomaly is apparently to be found in the competition between intramolecular and intermolecular hydrogen bond formation.

In the tautomerism of *o*-azophenols, the energetic relationships favour the formation of the carbonyl form to an even greater extent, again as a result of the production of an intramolecular hydrogen bond. As a result of this additional factor, tautomeric equilibrium is established between two isomeric forms even in solutions of 2-phenylazophenol [150]. It should be recognised that in *o*-phenylazophenol and *o*-phenylazonaphthols, intramolecular hydrogen bonding should also be shown by the phenolic form. It was first assumed [136,137,158,159] that these substances do not exhibit tautomeric properties, for the presence of the intramolecular hydrogen bond leads to the production of a mesomeric hybrid of the type:



that is, a delocalised hydrogen bond should be formed. Later spectroscopic studies [148,155,160] showed, however, that the system contains both isomers and that the intramolecular hydrogen bond is essentially static, leading to polarisation of the molecule and facilitating tautomerism.

The action of the other factors influencing the tautomeric equilibrium of *o*-azophenols is the same as that for *p*-azophenols. Table 3 gives data characterising the influence of the nature and position of substituents for 1-phenylazonaphth-2-ol. The effect differs little from those observed in the *para*-derivatives. The introduction of electron-donating substituents again displaces the equilibrium towards the azo-form and the introduction of electron-accepting substituents displaces it towards the hydrazo-form [155,156].

Table 4 gives data showing the influence of solvent on the equilibrium system for 1-(4-methoxy-3,5-dimethylphenylazo)naphth-2-ol and compares the results with those

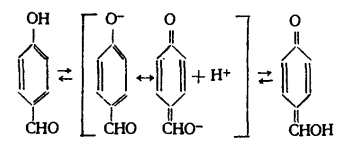
TABLE 4. Influence of solvent on the equilibrium for 1-(4-methoxy-3,5-dimethylphenylazo)-naphth-2-ol.

Solvent	Azo-compound $\epsilon_{azo}/\epsilon_{hydrazo}$	$CH_3COCH_2COOC_2H_5$ C_{enol}/C_{ketone}	$CH_3COCH_2COCH_3$ C_{enol}/C_{ketone}
Water	—	0.004	0.24
50% acetic acid	0.445	—	—
50% ethanol	0.556	—	—
CH_3COOH	0.570	0.061	2.8
75% ethanol	0.684	—	—
$CHCl_3$	0.764	0.089	3.8
87.5% ethanol	0.795	—	—
$C_6H_5NO_2$	1.040	—	—
C_2H_5OH	1.130	0.150	5.3
Pyridine	1.150	0.220	—
Benzene	1.160	0.220	5.7
CCl_4	1.350	—	—
n-Hexane	2.120	0.900	12.0

for the equilibrium constants (C_{enol}/C_{ketone}) for acetoacetic ester and acetylacetone [155]. There is a complete analogy in the influence of the substituents (Table 4). In all series the keto-structures are present in higher concentration in the more polar solvents.

5. EQUILIBRIUM PHENOL–QUINONOID TRANSFORMATIONS OF *p*-SUBSTITUTED PHENOLS

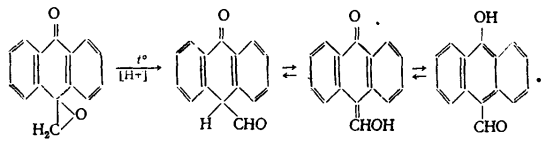
As already noted, the presence of electron-accepting groups in a phenol molecule should facilitate phenol–quinonoid tautomerism. In principle, this property may be shown by any phenol containing carbonyl, carboxyl, carbalkoxyl, nitrile, nitro- and other analogous groups in the *para*-position and, to a lesser extent, in the *ortho*-position. For example, for *p*-hydroxybenzaldehyde this transformation might be represented by the following equilibrium:



The displacement of the electrons in the aromatic ring under the influence of the negative conjugation effects of these substituents is generally insufficient, however, for the formation of a compound with a quinonoid bond system. Usually, this transformation requires the additional influence of other factors on the phenol molecule. The greatest influence in this direction is shown by steric hindrance, the decrease in the aromaticity of the phenol nucleus in condensed systems, and binding of the phenolic hydrogen by the medium. In the last, reversible equilibrium between the neutral phenolic form and a quinonoid anion may be established.

Published data show that the existence of the above tautomeric systems is possible. Thus study of the rearrangement of the epoxide of 9-methylene-10-anthrone [161,162] gave a yellow-orange substance with m.p. 206–208°, which according to the method of preparation and analysis should be 9-formyl-10-anthrone. The high acidity of the product (its strength is close to that of benzoic acid) indicates, however,

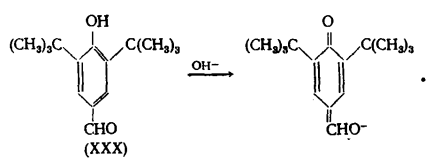
that it is present in equilibrium with the hydroxy-forms 9-formyl-10-anthrol and 9-hydroxymethylene-10-anthrone.



The existence of this ternary equilibrium was also confirmed by chemical and spectroscopic methods [162].

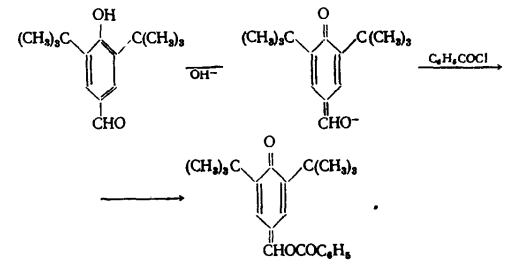
On going to the benzene series, it is difficult to reach definite conclusions regarding the tautomerism of hydroxybenzaldehyde. Thus Bartel [163], in a polarographic study of *p*-hydroxybenzaldehyde at pH 5.4–7.2 detected two polarographic waves similar to dissociation waves. These could not be attributed to ionised and un-ionised forms of the aldehyde, however, since the dissociation of *p*-hydroxybenzaldehyde in this pH range is too small. Even in a strongly alkaline medium, only neutral molecules are depolarised at the cathode. The existence of two waves might be attributed to tautomerism, but the absence of direct experimental data makes this suggestion extremely hypothetical.

The greatest quantity of material has appeared in connection with the study of the properties of phenols exhibiting steric hindrance. This is not surprising, in view of the general tendency for 2,6-disubstituted phenols and their derivatives to form stable quinonoid or quinolide structures [164–166]. The most typical compound in this respect is 3,5-di-t-butyl-4-hydroxybenzaldehyde (XXX), which exhibits extremely specific properties in an alkaline medium. Thus unlike the unsubstituted 2,6-di-t-butylphenol, it dissolves readily in alkalis, and this can be attributed only to the formation of a phenoxide ion in the isomeric dienone–enolate form. Careful neutralisation of alkaline solutions of this aldehyde leads to the quantitative separation of the aldehyde form [167]:



Spectroscopic studies [167,168] of alkaline solutions of (XXX) also indicate formation of the enolate form. When the aldehyde (XXX) is dissolved in alkalis, the absorption maximum in the ultraviolet spectrum (λ_{max} = 290 nm) is displaced towards longer wavelengths (λ_{max} = 370 nm). Absorption in this range is characteristic [169] of certain quinone methides and alkoxy-derivatives of quinone methides, with analogous structure. The infrared spectrum of an alkaline solution of (XXX) does not contain the band corresponding to an aromatic aldehyde, but shows an absorption band characteristic of conjugated carbonyl in quinone methide compounds, usually observed as an averaged band at 1618 cm^{-1} or split to form a doublet [170,171] in the region of 1610–1630 cm^{-1}. Finally, isolation of the sodium salt of 3,5-di-t-butyl-4-hydroxybenzaldehyde in crystalline form [167] showed that this compound also gives only the quinonoid bond system.

The quinonoid structure of the salt of the benzaldehyde (XXX) is also confirmed by chemical reactions. When the finely ground salt is heated in dry hexane with benzoyl chloride in a current of inert gas, the only product is 2,6-di-t-butylbenzoylhydroxyquinone methide [167]. The reaction with an alkaline solution of the benzaldehyde is analogous [168]:



These properties of 3,5-di-t-butyl-4-hydroxybenzaldehyde cannot be related to typical tautomerism, since in this example, as for phloroglucinol (see p. 820), the equilibrium apparently involves the un-ionised phenolic form and the dienone–enolate anion, whose formation is due to the transfer of the negative charge to the *p*-substituent from the strongly polarised π-electron bond.

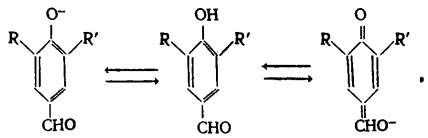
Properties analogous to those of 3,5-di-t-butyl-4-hydroxybenzaldehyde are shown by certain other 3,5-dialkyl-4-hydroxybenzaldehydes. Nikiforov and Ershov [167] recently studied the influence of alkyl substituents on the equilibrium between these aldehydes and their salts. The infrared spectra of solid specimens showed that the salts of 3,5-di-t-butyl-4-hydroxybenzaldehyde (XXX; R = R′ = CMe_3), 4-hydroxy-3,5-di-isopropylbenzaldehyde (XXXI; R = R′ = $CHMe_2$), and 5-t-butyl-4-hydroxy-3-methylbenzaldehyde (XXXII; R = CH_3, R′ = CMe_3) have a quinonoid structure, whereas salts of *p*-hydroxybenzaldehyde (XXXIV; R = = R′ = H) and 4-hydroxy-3,5-dimethylbenzaldehyde (XXXIII; R = R′ = CH_3) exist in the phenoxide form. Salts of the aldehydes (XXX), (XXXI), and (XXXII) in solution naturally may not have the classical quinonoid structure, since the distribution of the negative charge should be influenced significantly by the solvation of the entire molecule as a whole. There is no doubt, however, that the structure of these anions is close to the quinonoid structure, and this is responsible in particular for the ready solubility of these aldehydes in aqueous alkalis. This conclusion is confirmed by the ultraviolet spectra of the alkaline solutions and also by the equilibrium constants for the formation of the salts of 3,5-dialkyl-4-hydroxybenzaldehydes (Table 5).

For 3,5-dialkyl-4-hydroxybenzaldehydes exhibiting steric hindrance, the value of the constant is smaller and decreases monotonically with decrease in the steric hindrance at the phenolic hydroxyl, but it subsequently increases sharply on

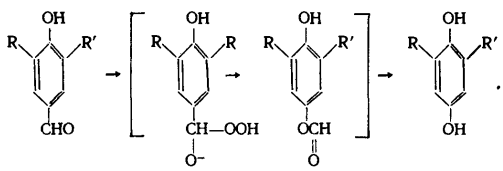
TABLE 5. Ultraviolet spectra and ionisation constants of 4-hydroxybenzaldehydes.

Compound No.	4-Hydroxy-3,5-dialkylbenzaldehyde	Ultraviolet spectra λ_{max} neutral	Ultraviolet spectra λ_{max} alkaline	Ultraviolet spectra Δλ	$10^9 K$
XXX	3,5-di-t-butyl	290	367	77	4.21
XXXI	3,5-di-isopropyl	290	356	66	3.80
XXXII	3-methyl-5-t-butyl	290	358	68	2.51
XXXIII	3,5-dimethyl	289	351	62	8.51
XXXIV	4-hydroxybenzaldehyde	285	336	51	11.48

going to the aldehyde with methyl substituents and the unsubstituted *p*-hydroxybenzaldehyde, and increases further



in the reverse order. For phenols as a whole, a decrease in dissociation constant with increase in the steric hindrance at the phenolic hydroxyl is characteristic. An analogous phenomenon is also observed in the formation of phenoxide salts of the hydroxyaldehydes (XXXIII) and (XXXIV), but the observed reverse relationship in compounds (XXX)–(XXXII) is due to the fact that the steric factor facilitates the phenol–dienone bond rearrangement and hence facilitates the formation of the quinonoid anion. These conclusions agree with data obtained from the infrared spectra of salts of *p*-hydroxybenzaldehydes and are confirmed by certain chemical reactions of these compounds, taking place in alkaline medium [172]. The most characteristic in this respect is Dakin's reaction. According to the mechanism accepted at present [173,174], this reaction passes through a stage involving the addition of hydrogen peroxide to the carbonyl group:



In practice, a marked decrease in the reaction rate is observed for hydroxyaldehydes with bulky alkyl substituents [172]. This is apparently due to the fact that these hydroxyaldehydes in alkaline medium (the conditions of Dakin's reaction) exist chiefly in the quinonoid–enolate form.

The influence of steric hindrance at the phenolic hydroxyl on the ease of formation of the quinonoid bond system has been followed most thoroughly in a study of the equilibrium between hydroxyphenyldiazonium salts and quinonediazides [174,175]:

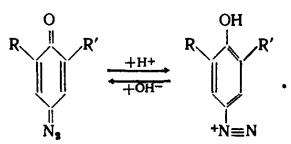


TABLE 6. Influence of substituents on the equilibrium conversion of quinone diazides into diazonium salts.

2,6-Dialkyl-p-quinone diazide	pK
p-Quinone diazide	3.19
2,6-Dimethyl	2.83
2-Methyl-6-t-butyl	2.72
2,6-Di-isopropyl	2.76
2,6-Di-t-butyl	1.65

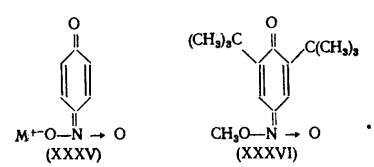
TABLE 7. Influence of *para*-substituents on the displacement of the absorption maximum in the ultraviolet spectrum of 4-substituted 2,6-di-t-butylphenols.

R	2,6-Di-t-butyl-4-R-phenol			R	2,6-Di-t-butyl-4-R-phenol		
	neutral, λ_{max}	alkaline, λ_{max}	$\Delta\lambda$		neutral, λ_{max}	alkaline, λ_{max}	$\Delta\lambda$
$C(CH_3)_3$	223	251	28	$COOC_2H_5$	261	324	63
CH_3	222	250	28	$COCH_3$	284	363	79
H	214	244	30	CN	252	307	55
Br	226	257	31	CHO	293	370	77
$CONH_2$	258	321	63	NO_2	325	450	125

The data [175] in Table 6 show that with increase in the steric hindrance at the phenolic hydroxyl, the equilibrium is displaced towards the formation of the quinonoid bond system, so that conversion of the quinonediazide into the diazonium salt requires an increasingly acidic medium. A characteristic feature is that the stability of the quinonediazides in the solid state increases in the same order [176].

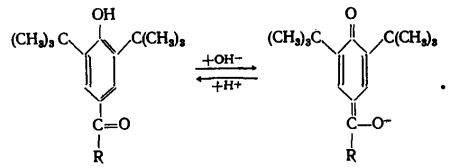
Since *o*-t-alkyl groups favour the formation of the quinonoid system to the greatest extent, a spectrophotometric study was made of the influence of various substituents on the behaviour of 4-substituted 2,6-di-t-butylphenols in alkaline medium [177,178]. The magnitude of the bathochromic shift (Table 7), which provides a criterion of the formation of a quinonoid system, increases with increase in the negative conjugation effect of the substituent, and differs considerably from the shift produced on the formation of ordinary phenoxide ions. In these examples we must naturally have in mind only the preferential location of the negative charge on the *para*-substituent. For phenols which do not contain alkyl substituents in the *ortho*-positions, the corresponding values of $\Delta\lambda$ are smaller, indicating greater delocalisation of the electron density throughout the molecule as a whole.

The greatest difference in absorption in alkaline medium is shown by 2,6-di-t-butyl-4-nitrophenol. The possibility of the reverse conversion of the neutral phenolic form of nitrophenols into the ionised quinonoid *aci*-form is also confirmed by certain chemical data. Thus *p*-nitrophenol salts which have been isolated are assigned the structure (XXXV): [179-181]

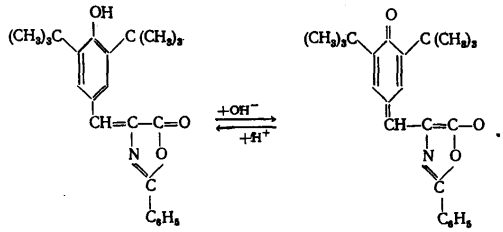


Methylation of 2,6-di-t-butyl-4-nitrophenol [177] gave a compound to which, on the basis of its chemical properties and spectroscopic data, was assigned the ether structure (XXXVI). It should be noted that in the methylation of 2,6-di-t-butyl-4-cyanophenol, only the normal *O*-methyl ether was isolated. The difference evidently excludes the influence of steric hindrance on the direction of the methylation of this nitrophenol. Finally, early papers [182] describe the methyl ether of the quinonoid form of *o*-nitrophenol. Unfortunately, the problems of reversible transformations in the nitrophenol series have as yet been insufficiently studied, so that no conclusions can be reached regarding the tautomeric transformation of nitrophenols.

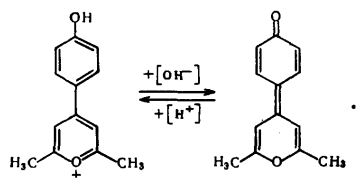
Spectroscopic data and the anomalous solubility in alkalis indicate [170,178,183] the existence of an equilibrium in the formation of salts of 4-benzoyl-, 4-cyano-, and 4-carbethoxy--2,6-di-t-butylphenols.



An analogous phenomenon is apparently observed in the formation of salts of 4-(3,5-di-t-butyl-4-hydroxybenzylidene)-2-phenyl-5-oxazolone [184]:

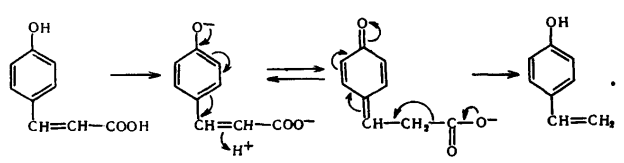


Very interesting behaviour in alkaline medium is shown by certain pyrylium salts containing phenolic substituents in the 4-position. Here the formation of the phenoxide ion should give a compound with a bipolar structure, with opposite charges on the oxygen atoms, established by the quinonoid conjugation extending over both rings [185].

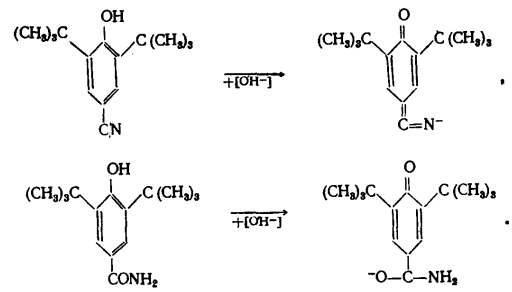


4-Substituted phenols on the whole show a distinct tendency to form a quinonoid bond system in reactions involving these substituents. These transformations are generally not tautomeric, however, but are related to the equilibrium between the ionised and un-ionised substance. Such transformations apparently explain the influence of the steric factor, facilitating formation of the quinonoid system, on the decarboxylation of *p*-hydroxycinnamic acids [186], the hydrolysis of *p*-hydroxybenzamides and nitriles [187], and the hydrolysis of the corresponding *N*-benzoyltyrosines and *N*-benzoyltyramines [188], taking place in alkaline medium.

In weakly alkaline solution, *p*-hydroxycinnamic acid is decarboxylated fairly rapidly, the reaction rate decreasing at pH < 9. This phenomenon can be attributed to the fact that protonation of the doubly-charged anion produces a quinonoid structure, which undergoes rapid decarboxylation:



The maximum corresponding to aromatic absorption in the ultraviolet spectrum of *p*-hydroxycinnamic acid in alkaline medium is displaced by 35 nm (310 nm → 345 nm), and this may indicate the presence of the quinonoid anion. This displacement is twice as large for 3,5-di-t-butyl-4-hydroxycinnamic acid (70 nm); the alkaline solution acquires a yellow colour, which disappears on acidification. The doubly-charged anion of this acid evidently exists in the quinonoid form. Its decarboxylation at pH 8.5 is 2.5 times faster than that of unsubstituted *p*-hydroxycinnamic acid [186]. An approximately analogous influence of the steric factor is observed in the hydrolysis of the amides and nitriles of the corresponding benzoic acids. Table 8 gives the rates of hydrolysis [187] of the benzamides and benzonitriles in alkaline medium. Comparison of the rates shows that the hydrolysis of 4-hydroxybenzamides and nitriles is 30 times faster than hydrolysis of their 4-hydroxy-3,5-di-t-butyl analogues. The rate of hydrolysis increases sharply for the 4-methoxy-derivatives. These facts are in good agreement with the assumption that an anion with the quinonoid structure exists under the conditions of the reaction:



The hydrolysis of *N*-benzoyltyrosines and *N*-benzoyltyramines is more complex [188]. These compounds are of interest since it is possible to establish a dienone structure with the formation of spirocyclic systems. Here again, the influence of the steric effect is clearly shown. Thus the rate of hydrolysis of 3,5-di-t-butyl-*N*-benzoyltyrosine is about half the rate of hydrolysis of *N*-benzoyltyrosine, and the corresponding rates for substituted and unsubstituted benzoyltyramines differ by a factor of 7.

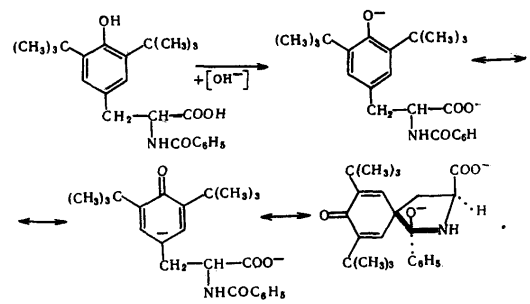
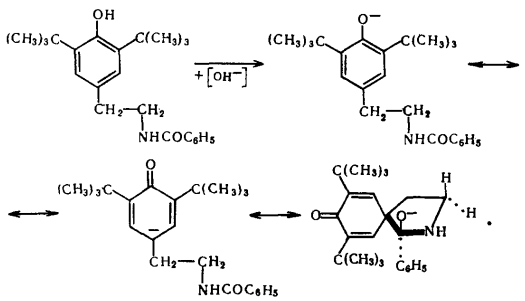


TABLE 8. Rate constants for the hydrolysis of benzamides and benzonitriles.

Compound		$10^6 K$, min^{-1}
Benzamides	4-hydroxy	63
	4-methoxy	963
	4-hydroxy-3,5-di-t-butyl	2
	4-methoxy-3,5-di-t-butyl	505
Benzonitriles	4-hydroxy	125
	4-methoxy	3000
	4-hydroxy-3,5-di-t-butyl	4
	4-methoxy-3,5-di-t-butyl	2000

The formation of a labile spirodienone should decrease the concentration of the *N*-benzoyl derivative, suitable for attack by an external base. The ratio of the rates shows that this factor increases in the tyramine series, since the formation of the spirodienone is then favoured to a greater extent in the hydrolysis of *N*-benzoyltyrosines:



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Tautomeric transformations in the phenol series are extremely interesting, since the phenomenon of tautomerism, which is widely encountered in organic chemistry, is here associated with the breakdown of an aromatic bond system. On the other hand, the questions examined above may also be useful for an understanding of many of the transformations of phenols and their derivatives, of definite practical importance. Unfortunately, most work on the tautomerism of phenolic compounds is chiefly qualitative in character. The investigation of strict quantitative relationships governing this phenomenon will undoubtedly be of considerable interest.

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ANOMALOUS POLYMERISATION OF SOME VINYL MONOMERS

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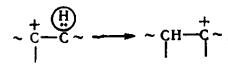
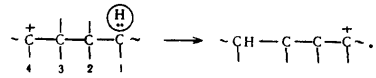
The problem of the regulation of the chain structure of polymers has always attracted the attention of many investigators. The discovery of stereospecific polymerisation was a great step forward in this direction. One of the interesting possibilities of regulating the chemical structure of macromolecules consists in changing the structure of the monomeric unit during the course of the polymerisation. This process, usually termed conversion or isomerisation polymerisation, results in the growth of the polymeric chain with simultaneous migration of a labile hydrogen atom or group of atoms.

Until now the most characteristic examples of anomalous polymerisation were observed mainly in cationic polymerisations, which are accompanied by the migration of a hydride ion [1]:



The hydride ion can migrate not only to neighbouring carbon atoms but also to those more distant:



Some authors [2,3] think that the transfer of hydrogen should be sequential: 1–2, 2–3, 3–4, etc.; others [4–6], that the migration takes place directly: 1–3, 1–4, etc.

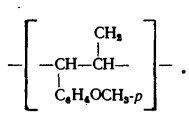
It is noteworthy that hydride transfer reactions have long been known in organic chemistry. Thus, to explain isomerisation, alkylation, cracking, and other reactions, many schemes involving intramolecular or intermolecular migration of hydrogen have been proposed [7–16].

The first suggestions about the possibility of hydrogen migration in polymerisation were made by Staudinger and Dreher [17] in 1935 in studying the polymerisation of β-methylstyrene and acetone. They performed the polymerisation in the presence of tin(IV) chloride and boron trifluoride in toluene at temperatures from 0° to -78° and suggested that polymerisation does not proceed in the usual way but with migration of a labile hydrogen of the methyl group, that is, 1,3-polymerisation occurs:

$$C_6H_5CH{=}CHCH_3 \rightarrow -C_6H_5CHCH_2CH_2 \longrightarrow -(C_6H_5CHCH_2CH_2-)_n.$$

Ozonation and pyrolysis were used to determine the structure of the polymers. Ozonation did not give results. β-Methylstyrene and acetone, and a little 1,4-diphenylbutadiene and 1,4-di-(*p*-methoxyphenyl)butadiene were detected in the products from pyrolysis at 300°.

The presence of these compounds in the pyrolysis products is attributed to the initial macromolecules having contained structures formed as a result of anomalous polymerisation. Later, a group of Hungarian scientists verified Staudinger and Dreher's results [18]. They polymerised anethole in benzene solution in the presence of tin(IV) chloride and titanium(IV) chloride at room temperature. On investigating the product, they concluded that the polyanethole had the general structure:



On comparing the results of the work of Staudinger and the Hungarian scientists, it is obvious that the conditions of the experiments were not identical; Staudinger carried out the polymerisation at low catalyst concentrations; the Hungarians studied the polymerisation at room temperature with high catalyst concentrations.

Italian scientists investigated the polymerisation of anethole in the presence of aluminium chloride, titanium(IV)

TABLE 1. Polymerisation of anethole on boron trifluoride.

Temperature, °C	Solvent	Degree of polymerisation	No. of C–CH_3 groups present in one molecule	Proportion of 1,2-structure in polymer, %
+15	ether	5.6	3.2	57
+15	ether	5.9	3.7	63
+15	dioxan	4.4	2.7	64
0	ether	7.1	5.5	77
−15	ether	8.3	6.9	83
−77	ether	9.4	7.6	81
−77	petroleum ether	11.2	9.8	87

chloride, and boron trifluoride at various temperatures [19,20]. By using the molecular weight of the polymers and the chemically determined number of CH_3–C groups in the molecule [20], the authors showed the presence of a 1,3-structure in polyanethole. Table 1 shows that a rise in temperature favours 1,3-polymerisation (correspondingly, the proportion of 1,2-structure in the chain decreases).

Kennedy [21] repeated the experiments on the polymerisation of β-methylstyrene and concluded, from the infrared spectra of the polymer obtained in methyl chloride in the presence of aluminium chloride at -60°, that it has the ordinary structure:

$$-\left[\begin{array}{l} \quad\quad CH_3 \\ -CH-CH- \\ \quad | \\ \quad C_6H_5 \end{array}\right]-.$$

Hence the contradictory results do not allow a definite conclusion to be drawn concerning the nature of the polymerisation of β-methylstyrene and anethole.

In 1955, the attention of our laboratory was drawn to the fact that in poly-(2-methylprop-1-ene) (polyisobutylene) obtained on a Ziegler catalyst the ratio of the number of CH_2 groups differed from the ratio of these groups in ordinary poly-(2-methylprop-1-ene): [22]

$$CH_2{=}C(CH_3)_2 \rightarrow -CH_2C(CH_3)_2CH_2C(CH_3)_2-, \quad (1)$$

usual structure of poly-(2-methylprop-1-ene)

$$CH_2{=}C(CH_3)_2 \rightarrow -CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2-. \quad (2)$$

anomalous structure of poly-(2-methylprop-1-ene)

This observation could be interpreted as the polymerisation of 2-methylprop-1-ene on the triethylaluminium + + titanium(IV) chloride catalytic system yielding an anomalous polymer due to hydrogen migration. Because of this a detailed study of the polymerisation of 2-methylprop-1--ene was undertaken. The task was to find conditions under which the migration rate of the labile hydrogen atom would be commensurate with the rate of the ordinary vinyl polymerisation.

Infrared spectroscopy and an analysis of molecular weight distribution were used to determine the structure of the poly-(2-methylprop-1-ene). [23]

The usual method of studying polymers on the ultracentrifuge — from the development of sedimentation diagrams — seemed inapplicable to the poly-(2-methylprop--1-ene)s synthesised; therefore a method was used which allowed the mean molecular weight of any soluble polymers to be determined directly by analysis of the distributed concentrations in the solid layer of a sedimentation cell during the period before the sedimentation equilibrium was established [24].

The sedimentation measurements were made in a large oil ultracentrifuge at 30 000 rev min^{-1}. The molecular weight distribution curves for specimens of poly-(2-methylprop-1-ene) were constructed by use of the weight average M_w and the z-average M_z molecular weights and some model function [25] (see Fig. 1 and Table 2). The correct choice of model function was confirmed for four specimens by a series of experiments which included the measurement of the molecular weights of the specimens by hydrodynamic properties: sedimentation coefficients, diffusion coefficients, and characteristic viscosity [25]. The distribution function of one of the specimens (1) differed significantly from those of the others. It is noteworthy that this specimen was obtained at an Al/Ti ratio of 5 : 1, that is, when the infrared spectra indicate the formation of anomalous structural fragments in the poly-(2-methylprop-1-ene). The infrared spectra showed that an increase in the number of CH_2 groups increases with increased Al/Ti ratios. This indicates the commencement of parts of a new structure of the poly-(2-methylprop-1-ene), where the CH_3/CH_2 ratio is < 2, Eqn. (2), whereas in the ordinary poly-(2-methylprop-1-ene) it equals 2, (Eqn. (1).

Hence two independent physical methods showed the presence of anomalous structural groupings in specimens of poly-(2-methylprop-1-ene) obtained with an excess of trialkylaluminium in the catalyst.

The formation of such structures was observed at ratios Al/Ti > 3. The polymers obtained at other ratios of the components of the catalytic system have the ordinary structure. This has also been shown by American investigators [26], who did not observe an anomalous structure in

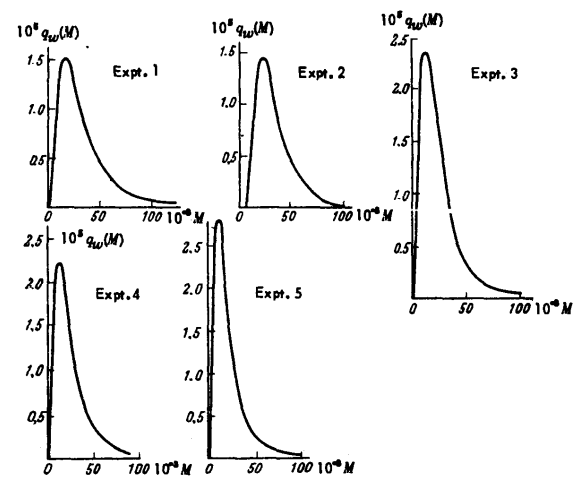


Fig. 1. Molecular weight distribution curves for poly-(2-methylprop-1-ene).

TABLE 2. Functions of the molecular weight distribution of poly--(2-methylprop-1-ene).

Specimen	M_z	M_w	M_n	M_e	$M_{SD_{sm}}$	$M_s[\eta]$	M_z/M_w	β	$10^5 g_w(M_e)$
1	60600	36600	22000	16500	37100	40000	1.66	1.02	2.51
2	42900	38400	26000	22800	21600	24400	1.12	0.71	3.03
3	47300	27200	15000	11600	14100	18500	1.74	1.06	3.55
4	49100	28100	16000	12100	14500	13500	1.74	1.06	3.3
5	38900	23500	14100	10650	6900	3800	1.66	1.02	3.9

the poly-(2-methylprop-1-ene) which they obtained on a Ziegler catalyst at ratios of Al/Ti = 2 or less.

After the publication of a paper on the conversion polymerisation of 2-methylprop-1-ene[22] attention was directed to the possibility of carrying out the 1,3-polymerisation of propene[27]. It was suggested that, depending on the reaction conditions and the catalyst used, the polymerisation can be directed to the formation of a 1,2-structure, Eqn.(3); a 1,3-structure, Eqn.(4); or their mixture, Eqn.(5):

$$CH_2{=}CH(CH_3) + [Cat] \rightarrow \sim CH_2CH(CH_3)\ldots[Cat], \quad (3)$$

$$\sim CH_2{-}\overset{\oplus}{C}H \ldots [Cat] \longleftrightarrow \sim CH_2{-}CH_2{-}CH_2\ldots[Cat], \quad (4)$$

$$\sim (CH_2)_nCH(CH_3)\,CH_2\,(CH_2)_nCH(CH_3)\,CH_2{\sim}. \quad (5)$$

The realisation of such an anomalous polymerisation of propene, as well being of exceptional scientific value, is of great practical interest, since with its aid a single monomer (propene) can yield a series of polyalkenes of different structure and properties. The recently published investigation of the 1,3-polymerisation of propene and study of the properties of the polymer obtained therefore merits attention[28].

The polymerisation was carried out in the presence of the catalytic system VCl_4.Fe(acetylacetonate) + $Al(C_2H_5)_3$. Infrared spectroscopy was used to identify the structure of the polymers. It was found that the degree of migration of hydrogen during polymerisation depends on the solvent. When the polymerisation is carried out in n-heptane, a polymer with the usual 1,2-structure is obtained. In benzene and its derivatives a polymer is obtained with the structure of a copolymer of ethylene and propene. An increase in the pressure and temperature of the reaction brought about an increase in the amount of copolymer. Polyethylene was obtained from propene when the polymerisation was carried out in dichloroethane. The X-ray diagram of the product showed that it has a crystal structure similar to that of polyethylene.

The conversion polymerisation of 3-methylbut-1-ene has been studied most[29,30]. The polymerisation was performed at low temperatures in ethyl chloride solution; aluminium chloride was used as catalyst. The polymer was obtained as colourless crystals, m.p. 55°, with molecular weight ~ 55 000. The infrared and NMR spectra of this polymer differed from those obtained from the polymer produced on a Ziegler catalyst. The authors proposed the following polymerisation mechanism: the cation attacks the molecule of the monomer, forming a secondary carbonium ion:

$$K^+ + CH_2{=}CH(CH(CH_3)_2) \rightarrow K{-}CH_2{-}\overset{+}{C}H(CH(CH_3)_2).$$

The labile hydrogen at the tertiary carbon atom migrates to the secondary carbonium ion as a hydride ion, during which process an energetically favoured tertiary carbonium ion is formed:

$$K{-}CH_2{-}\overset{+}{C}H(CH(CH_3)_2) \rightarrow K{-}CH_2{-}CH_2 + CH_2{=}CH(CH(CH_3)_2) \rightarrow$$

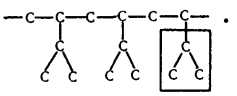
$$\rightarrow K{-}CH_2{-}CH_2{-}C(CH_3)_2{-}CH_2{-}\overset{+}{C}H(CH(CH_3)_2) \rightarrow K{-}CH_2{-}CH_2{-}C(CH_3)_2{-}CH_2{-}CH_2{-}\overset{+}{C}(CH_3)_2, \text{ etc.}$$

For a more convincing proof of the presence of the anomalous structure in the polymer synthesised on aluminium chloride the normal poly-(3-methylbut-1-ene) was synthesised by directed 1,2-polymerisation of isoprene with subsequent hydrogenation[31]:

$$CH_2{=}CH(C(CH_3){=}CH_2) \rightarrow -(-CH_2{-}CH(C(CH_3){=}CH_2)-)_n- \xrightarrow{+H_2} -(-CH_2{-}CH(CH(CH_3)_2)-)_n-.$$

The NMR spectrum of this product agreed with that of poly-(3-methylbut-1-ene) obtained on Ziegler catalyst and differed from that of poly-(3-methylbut-1-ene) synthesised on cationic catalysts. The relative proportions of anomalous and ordinary structures were determined by pyrolysis of the polymer with subsequent quantitative analysis of the gaseous products by gas chromatography and investigation of the liquid products of the pyrolysis by infrared spectroscopy. Analysis of the gaseous pyrolysis products of an isotactic polymer obtained on a Ziegler catalyst and of a hydrogenated 3,4-polyisoprene showed concentrations of 65.4 and 66.7 mole % C_3 fragments, which are formed only in the ordinary polymerisation of 3-methylbut-1-ene:

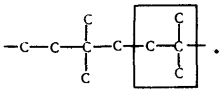
1,2-polymer



C_3 fragments

In the pyrolysis of anomalous poly-(3-methylbut-1-ene), synthesised in the presence of cationic catalysts at -96°, only 20.7 mole % C_3 fragments and 30 mole % 2-methylprop-1-ene C_4 fragments are formed:

1,3-polymer



C_4 fragments

The proportions of 2-methylprop-1-ene fraction in the pyrolysis of an isotactic polymer and of hydrogenated polyisoprene are 9.1 and 5.3 mole % respectively. Evidently the ratio of the amounts of C_3 and C_4 fragments depends on the presence in the polymer of ordinary and anomalous structures.

The amount of 1,3-structure in polymers obtained on cationic catalysts at temperatures from -78° to -96° reaches 70%. The infrared spectra of the liquid pyrolysis products of poly-(3-methylbut-1-ene) confirm the gas chromatographic results.

Additional proof of the presence of a 1,3-structure in poly-(3-methylbut-1-ene) is obtained in the polymerisation of 1,1-dimethylcyclopropane on aluminium bromide[32]:

$$CH_2{<}C(CH_3)_2{<}CH_2 \rightarrow -(-CH_2CH_2C(CH_3)_2-)-.$$

The infrared spectrum of the polymer thus obtained agrees completely with the spectrum of anomalous poly-(3-methylbut-1-ene).

Edwards and Chamberlain investigated the migration of hydride ion in the polymerisation of methylalk-1-enes of the type:

$$CH_2{=}CH{-}(CH_2)_m{-}\overset{\oplus}{C}H(CH_3)_2,$$

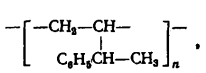
on cationic catalysts[33] and found that for $m = 0$ — for 3-methylbut-1-ene — 1,3-polymerisation proceeds throughout the entire temperature range studied (from 0° to -73°). For $m = 1$, the transfer path of the hydride ion is longer; therefore polymerisation at 0° leads to the production of only an insignificant amount of the 1,4-polymer. However, on lowering the temperature to -73° 1,4-polymerisation predominates.

For $m = 2$ and 0°, 1,5-polymerisation is almost absent; at -73°, <50% of the 1,5-polymer is formed. This shows that at lower temperature the migration of hydride ion is easier than ordinary vinyl polymerisation. Apparently, as the temperature is raised the growth rate increases more rapidly than the hydride ion migration rate, and consequently the growth activation energy is greater than the hydride ion migration activation energy.

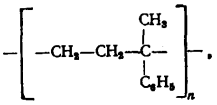
Somewhat in contradiction to Edwards and Chamberlain's results is the work of Goodrich and coworkers[34], in which it was shown that a low temperature is not necessary for the anomalous polymerisation of 4-methylpent-1-ene. These authors carried out the polymerisation in the temperature range from 0° to 60° in n-heptane solution; as catalyst, they used certain derivatives of transition metals and alkylaluminium halides.

The principal results of the workers cited above[29-33] were recently confirmed again[35]. The structure of poly-(3-methylbut-1-ene), poly-(4-methylpent-1-ene), and poly-(6-methylhept-1-ene), obtained in polymerisation on Friedel–Crafts catalysts in ethyl chloride and heptane at temperatures from 0° to -78° was studied. An anomalous structure was present in all these polymers and it was found that the ratio of anomalous structure to ordinary: (1) is independent of the type of catalyst; (2) increases with the dielectric constant of the solvent; (3) increases at lower temperatures.

Mention must also be made of work[36] on the polymerisation of 3-phenylbut-1-ene. When this compound is polymerised in ethyl chloride solution at -78° in the presence of aluminium chloride, in addition to the polymer of expected structure:

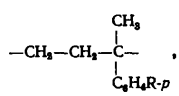


a polymer with the 1,3-structure:



is obtained in 56% yield. The structure of the polymer was determined with the aid of NMR and infrared spectra.

It is interesting that according to the infrared spectrum the polymer contains mono- and di-substituted benzene rings:



where R = H or $CH_3-CH-CH-CH_3$ (with C_6H_5 on the second CH), that is, alkylation of the benzene ring takes place in addition to the anomalous polymerisation. However, during alkylation the isomerisation of the secondary and the (energetically more favourable) tertiary carbonium ions does not take place. The authors explain this by the fact that under certain conditions the rate of alkylation of the benzene ring can be greater than the rate of rearrangement.

From certain other monomers which are apparently capable of polymerisation with migration of a hydride ion, mention may be made of the compounds of type:

$$\text{cyclo-}C_6H_{11}[CH_2]_nCH{=}CH_2 \text{ and cyclo-}C_5H_9[CH_2]_nCH{=}CH_2.$$

These substances have similar structure fragments to compounds of the 3-methylbut-1-ene type and therefore should be capable of anomalous polymerisation. The anomalous polymerisation of these cyclic monomers makes possible the introduction into the polymeric chain of the cyclohexyl or cyclopentyl ring, which should markedly change the properties of the polymer. Ketley and Ehrig[37] studied the polymerisation of such a type of monomer. The infrared spectra of poly(vinylcycloalkanes) and poly(allylcycloalkanes) obtained on Ziegler–Natta catalysts showed that the polymers have the normal structure (Fig. 2).

The absorption bands characteristic of different sequences of methylene groups for the polymers obtained on Friedel–Crafts catalysts are shown in Table 3. The presence of absorption bands characteristic of the groups

$$-(-CH_2-CH_2-)- \text{ and } -(-CH_2-CH_2-CH_2-)-,$$

which belong respectively to poly(vinylcyclohexane) and poly(allylcyclohexane) (Fig. 3), obtained on cationic catalysts and the absence of these bands from the spectra of the polymers obtained on Ziegler–Natta catalysts, shows that in polymerisation on cationic catalysts hydrogen migration

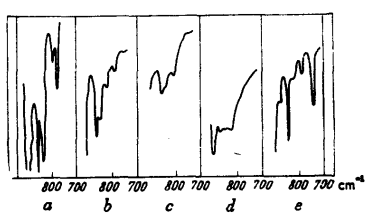


Fig. 2. Infrared spectra of polymers obtained on Ziegler–Natta catalysts:
a) vinylcyclohexane; *b*) allylcyclohexane; *c*) vinylcyclopentane; *d*) allylcyclopentane; *e*) 5-cyclohexylpent-1-ene.

TABLE 3. Absorption bands of the methylene groups of polycyclohexylalkenes and poly(cyclopentylalkenes) obtained on Friedel–Crafts catalysts.

Polymer	Absorption band, cm⁻¹	Fragment of structure
Poly(vinylcyclohexane)	748	$-(-CH_2-)_2-$
Poly(allylcyclohexane)	725	$-(-CH_2-)_3-$
Poly(vinylcyclopentane)	—	—
Poly(allylcyclopentane)	750	$-(-CH_2-)_2-$
Poly-(5-cyclohexylpent-1-ene)	721	$-(-CH_2-)_3-$

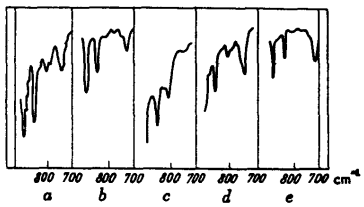
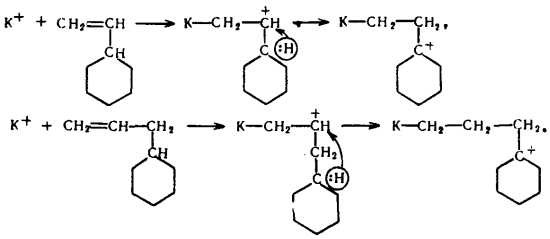


Fig. 3. Infrared spectra of polymers obtained on Friedel–Crafts catalysts:
a) vinylcyclohexane; *b*) allylcyclohexane;
c) vinylcyclopentane; *d*) allylcyclopentane;
e) 5-cyclohexylpent-1-ene.

takes place, leading to the formation of anomalous polymers:



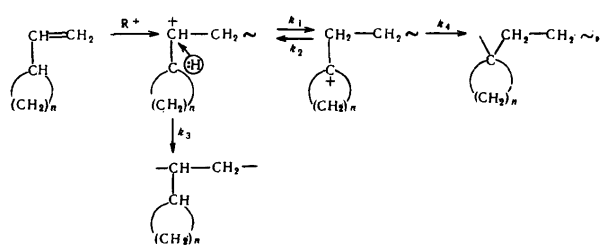
The strong absorption band at 721 cm^{-1} in poly-(5-cyclohexylpent-1-ene) obtained on cationic catalysts supports the structure:

$$-CH_2CH_2CH_2CH_2CH_2C_6H_{10}-.$$

Poly-(5-cyclohexylpent-1-ene) obtained on a Ziegler–Natta type catalyst has an absorption band at 730 cm^{-1}, which corresponds to

$$-(-CH_2-CH_2-CH_2-)-$$

in the lateral cyclohexylpropyl groups. Poly(vinylcyclopentane) obtained on cationic catalysts does not have an absorption band in the range 740–745 cm^{-1}. Hence it can be concluded that this is an ordinary 1,2-polymer. The fact that isomerisation polymerisation takes place with vinylcyclohexane, whereas for vinylcyclopentane there is the usual 1,2-polymerisation, is rather unexpected. The authors propose the following scheme of polymerisation of this type of monomer:



where k_3 should be approximately the same for cyclohexyl and cyclopentyl compounds. It can therefore be assumed that the ion formed initially during the polymerisation of vinylcyclopentane is not isomerised. When it is subjected to isomerisation then the carbonium ion which is formed is less active than in vinylcyclohexane.

The 750 cm^{-1} absorption band in the infrared spectrum of poly(allylcyclopentane) obtained on a Friedel–Crafts catalyst corresponds most likely to the $-(CH_2-CH_2-)$ groups, and not $-(CH_2-CH_2-CH_2)-$. Therefore the anomalous structure of this polymer can be represented as $-CH_2CH_2CH(C_5H_9)-$. The chain growth of poly(allylcyclopentane) will proceed with greater probability with the participation of a secondary carbonium ion situated close to the ring.

Simultaneously with Ketley and Ehrig's work appeared that of Kennedy and coworkers, which was also devoted to an investigation of the anomalous polymerisation of vinylcyclohexane[38]. The polymerisation of vinylcyclohexane was studied from -144° to +7° (catalyst, $AlCl_3$; the solvent, ethyl chloride) and from 60° to 85° (catalyst, $AlEt_3 + TiCl_4$; solvent, n-heptane). From the infrared and NMR spectra, the authors concluded that the 1,3-structure predominates in polymers obtained on aluminium chloride at temperatures below -100°. The melting points of poly(vinylcyclohexane)s containing chains with an anomalous structure were considerably lower (70–120°) than those of polymers with a 1,2-structure (200°).

The results suggest that isomerisation polymerisation of both 3-methylbut-1-ene and vinylcycloalkanes depends on the ability of the corresponding hydrogen atom to migrate, the stability of the tertiary carbonium ion formed, and its activity with respect to the monomer molecules.

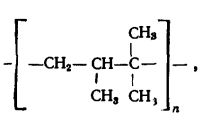
It must be noted that in addition to the communications devoted to polymerisation with hydride ion migration there are some reports of the possibility of migration of other groups or atoms. One of the first of these was made by Meier[39], who advanced the possibility of the migration of a methyl group in the polymerisation of 3,3-dimethylbut-1-ene:

$$CH_2{=}CHC(CH_3)_3 \xrightarrow{+A} \bar{A}\cdot CH_2\overset{+}{C}HC(CH_3)_3 \longrightarrow \bar{A}\cdot CH_2CH(CH_3)\overset{+}{C}(CH_3)_2 \longrightarrow \text{polymer.}$$

However, he did not produce experimental proof of the proposed scheme.

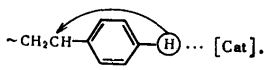
Edwards and Chamberlain suggested that in view of the similarity in the structures of 3-methylbut-1-ene and 3,3-dimethylbut-1-ene, polymerisation by migration of a methyl group (analogous to the hydrogen atom in 3-methylbut-1-ene) could be expected[33]. However, they did not succeed in obtaining a 1,3-polymer in the polymerisation of 3,3-dimethylbut-1-ene in the presence of aluminium chloride at 0°. The authors attributed their failure to steric hindrance.

Kennedy and coworkers repeated this work[40] and suggested that the reason for Edwards and Chamberlain's failure is the high rate of chain breaking after the migration of the methyl group. The authors assumed that the reaction of chain transfer or breaking requires a greater activation energy than isomerisation and growth and therefore the migration of the methyl group will take place more readily at a lower temperature. When the polymerisation of 3,3-dimethylbut-1-ene was carried out in the temperature range from -30° to -130° a trimer of 3,3-dimethylbut-1-ene was obtained. Polymerisation at a lower temperature (-130°) led to the production of an amorphous polymer. On the basis of the infrared and NMR spectra, Kennedy and coworkers proposed the following structure for this polymer:



that is, it can be assumed that in the polymerisation at -130°, migration of the methyl group precedes the growth

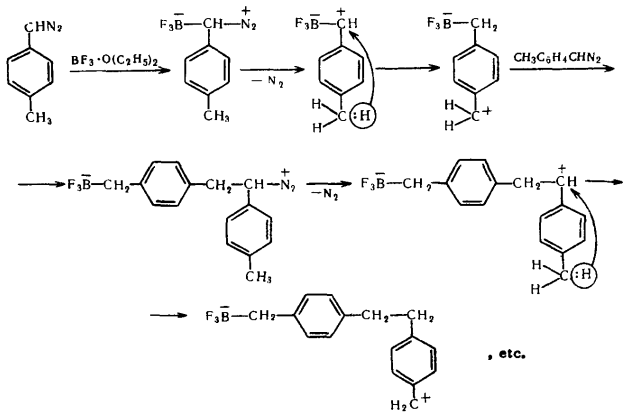
reaction, forming the energetically more favourable tertiary carbonium ion. The possibility of anomalous polymerisation of styrene with inclusion of the benzene ring in the main polymeric chain has been suggested[27]:



The first experimental proof of this hypothesis was obtained in our laboratory[41]. In the polymerisation of styrene on the system $AlEt_3$ + $VOCl_3$ a polymer was obtained from which a small fraction insoluble in benzene, with m.p. 310–315°, could be isolated. An absorption band with maximum 809 cm^{-1} was observed in the infrared spectrum of this polystyrene; it is characteristic for the 1,4-disubstituted benzene ring.

It was suggested that in the polymerisation of styrene transfer of an active centre in the *ortho*- or *para*-position to the vinyl group occurs. During this reaction the benzene or quinonoid structures are included in the main chain of the polymeric molecule. However, later investigations showed that such a possibility is ruled out.

Korshak and coworkers[42] obtained polymers including benzene rings by a somewhat unusual route. They observed that in the decomposition of phenyldiazomethane in the presence of $BF_3.O(C_2H_5)_2$ a polymer containing methylene and phenylene groups in the main chain is formed. The authors explained this fact by the partial isomerisation of phenyldiazomethane during polymerisation. The study of the infrared and NMR spectra of polymers obtained during the decomposition of 4-methylphenyldiazomethane in the presence of $BF_3.O(C_2H_5)_2$ showed the high concentration of methylene groups in the polymer. The conclusion was drawn that in the decomposition of 4-methylphenyldiazomethane formation of a polymer containing methylene and phenylene groups takes place. A mechanism for the polymerisation is proposed in which the transfer of a hydride ion to the cation being formed is realised:



In some instances the realisation of anomalous addition can have practical value. An example of this has already been mentioned — the production of copolymers of ethylene and propene as a result of the conversion polymerisation of propene.

It is possible that a way will be found of carrying out the conversion polymerisation in those instances where the direct synthesis of the polymer from the monomer by ordinary means is impossible, for example, with poly(vinyl alcohol). The conversion polymerisation of acetaldehyde can in principle lead to the direct formation of polyvinyl alcohol:

$$CH_3CHO \rightarrow -CH_2-CH(OH)-.$$

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β-ELIMINATION IN THE β-SUBSTITUTED PROPIONIC ACID SERIES

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CONTENTS

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It has long been known that β-substituted propionic acids and their derivatives have a tendency to undergo β-elimination:

$$ACH_2CH_2X \rightarrow AH + CH_2{=}CHX$$

where A = halogen, HO, RO, RS, RSO_2, H_2N, RNH, or $(R)_2N$, etc., and X = COOH, COOR, $CONH_2$, or CN.

These reactions are of both theoretical and practical interest. However, up to recently information on this subject had not been summarised. The present review covers factual information on the β-elimination of β-substituted propionic acids, their esters, amides, and nitriles.

1. β-SUBSTITUTED PROPIONIC ACIDS

β-Halogenopropionic acids are converted into acrylic acid by distillation[1]; by heating under pressure[2] or under vacuum[3]; by heating in the presence of activated charcoal[3] or aluminium oxide[4]; by boiling with water[5] or with aqueous solutions of alkalis[5-11]; and by the action of sodium carbonate[11], lead oxide[11-13] or carbonate[12], alkali metal alkoxides[6], sodium acrylate[14], or diethylaniline[9,10]. Several attempts to synthesise β-alanine and its methyl ester from β-bromopropionic acid led to the preparation of acrylic acid[15]. When β-iodopropionic acid is treated with an excess of silver oxide, a polymer of acrylic acid is formed[16-18].

In 1862 Beilstein noted[12] that, when salts of β-hydroxypropionic acid are heated to 200–250°, salts of acrylic and diacrylic acid are formed. Later this reaction was also observed by Wislicenus[13,19]. Acrylic acid is formed when β-hydroxypropionic acid is heated to boiling, or when the acid itself, or its salts, is distilled with sulphuric acid[12,13,19-22]. When β-hydroxypropionic acid is evaporated with hydrochloric acid, a polymer of acrylic acid is formed[16-18]. Acrylic acid is obtained from a mixture of β-hydroxypropionic acid, diacrylic acid, and acrylic acid polymer[23], and also from 2-hydroxypropiononitrile[24-28].

At 190–225°, and in the presence of alkali or alkaline-earth salts of the same acids, β-alkoxypropionic acids (containing C_1 to C_{17} alkoxy-groups) give acrylic acid in good yield[29]. When β-ethoxypropionic acid is heated in the presence of *p*-toluenesulphonic acid and hydroquinone, a mixture of acrylic acid and its ethyl ester is formed[30,31]. According to the patent literature, 2-dicarboxydiethyl ether gives acrylic acid when it is treated in the gas phase at 150–185° with activated charcoal soaked in phosphoric acid[32]. In an alkaline medium, β-carboxyethyl esters of monohydric and dihydric phenols give decarboxyethylation products[33-38]. When heated for a short time to 180–190° in the presence of hydroquinone, β-acetoxypropionic acid decomposes according to the following reaction[39]:

$$CH_3COOCH_2CH_2COOH \rightarrow CH_3COOH + CH_2{=}CHCOOH.$$

The yield of acrylic acid is 77%. The removal of the β-carboxyethyl group in esters of phosphoric acid[40-43] has been studied. Methods of synthesising α- and β-substituted acrylic acids from α- and β-substituted β-hydroxypropionic acids and their esters at the hydroxy-group have been developed[44-59].

When 2-carboxyethyl aryl sulphones are boiled with 10% sodium hydroxide, cleavage occurs according to the following scheme[60]:

$$ArSO_2CH_2CH_2COOH \rightarrow ArSO_2H + CH_2{=}CHCOOH.$$

Mulder[61] observed that β-aminopropionic acid decomposes into acrylic acid and ammonia when it is heated to about the melting point. β-Diethylaminopropionic acid decomposes in the same way (160°):[62]

$$(C_2H_5)_2NCH_2CH_2COOH \rightarrow (C_2H_5)_2NH + CH_2{=}CHCOOH.$$

When heated to its melting point, the betaine of β-trimethylaminopropionic acid gives ammonium acrylate[63]. The decarboxyethylation of *N*-(2-carboxyethyl)-α-amino-acids has been studied[34]. Heating of 2,2'-dicarboxydiethylamine with phthalic anhydride leads to the formation of *N*-(2-carboxyethyl)phthalimide and acrylic acid in quantitative yield[64].

Attempts to cyclise *N*-(2-carboxyethyl)-*N*-acycl-*p*-anisidines to the corresponding quinolones led to decarboxyethylation[65]. When *N*-(2-naphthyl)-β-aminopropionic acid is heated for 2–3 min at 220°, 1-naphthylamine and acrylic acid are formed[66].

According to Rodionov and coworkers [67], when β-(2-naphthyl)-β-(3-phenylureido)propionic acid is heated with dilute hydrochloric acid, instead of cyclising to the corresponding dihydrouracil, it sometimes forms β-(2-naphthyl)acrylic acid. An attempt to obtain 1-methyl-4-naphthyl-2-thiodihydrouracil from β-(methylamino)-β-(2-naphthyl)propionic acid by heating the latter with potassium thiocyanate in the presence of hydrochloric acid was not successful; β-(2-naphthyl)acrylic acid was the only product isolated from the reaction mixture. In some instances, the cyclisation of β-alkyl- and β-aryl-β-guanidinopropionic acids leads to the elimination of guanidine and the formation of an αβ-unsaturated acid [67,68]. An attempt has been made to synthesise β-(2-thienyl)-β-alanine by the acid hydrolysis of 6-(2-thienyl)dihydrouracil, but β-(2-thienyl)acrylic acid was obtained instead of the amino-acid [69].

When the products of *NN*-dicarboxyethylation of benzenesulphonamide [70], *p*-toluenesulphonamide [71], and sulphanilamide [72] are heated with a 10% aqueous solution of potassium hydroxide, one of the 2-carboxyethyl groups is removed and *N*-monocarboxyethyl derivatives of aryl sulphonamides are formed in 60 and 86% yield:

$$ArSO_2N(CH_2CH_2COOH)_2 \rightarrow ArSO_2NHCH_2CH_2COOH + CH_2{=}CHCOOH.$$

Quantitative elimination of the 2-carboxyethyl group is achieved by treating an alkaline solution of β-indol-1-ylpropionic acid with water vapour superheated to 250–270°. [73] Later this process was observed under analogous conditions by other workers [74]. If water vapour superheated to 280° is passed for 30–40 min through a solution of 1,3-di-(2-carboxyethyl)indole in 50% potassium hydroxide, β-indol-3-ylpropionic acid is formed in 82% yield [75]. 1,3-Di-(2-carboxyethyl)-2-methylindole behaves in the same way under these conditions [75], the yield of its *N*-decarboxyethylated product being 80%. From the foregoing it is clear that the 2-carboxyethyl group can be eliminated if it occurs at the 1-position in indole, but it is stable if it occurs at the 3-position [73–78].

When distilled under reduced pressure, β-indazolylpropionic acid decomposes with the formation of indazole and acrylic acid [79]. Efros and Porai-Koshits obtained benzimidazole by heating β-carboxyethylated benzimidazole with aqueous solutions of acids or alkalis [80]. They were not, however, able to remove the 2-carboxyethyl group from carboxyethylated 2-methylbenzimidazole. When derivatives of pyridine containing a 2-carboxyethyl group at the ring-nitrogen atom are heated above the melting point, or treated with aqueous sodium hydroxide solution, they decompose with the formation of pyridine, 2- and 3-hydroxy-, 2-amino- and 4-methyl-2-amino-pyridines, and also acrylic acid [35,81–83].

Pyrolysis of, or the action of concentrated aqueous sodium hydroxide on, *N*-(2-carboxyethyl)pyrid-2-one gives the decarboxyethylation product and acrylic acid [84]. Attempts to convert some substituted *N*-(2-carboxyethyl)-4-keto-1,2,3,4-tetrahydroquinolines into the corresponding *N*-ethyl-4-keto-1,2,3,4-tetrahydroquinolines have not been successful; decarboxyethylation occurred under all experimental conditions instead of the expected decarboxylation [85].

There are also other references to decarboxyethylation [35,86–93], and to the removal of one aryl group from ββ β-triaryl-substituted propionic acids [94–96]. The bond of the 2-carboxyethyl group with the silicon atom is stronger than the bond of other alkyl groups with this atom [97–100].

2. ESTERS OF β-SUBSTITUTED PROPIONIC ACIDS

Esters of acrylic acid are formed from esters of β-halogenopropionic acids by distilling the latter with concentrated sulphuric [101,102] or phosphoric acid [101]; by heating them with aqueous [103] or alcoholic [103,104] solutions of alkali; by heating them with anhydrous sodium carbonate [102], diethylaniline [8,9], quinoline [105,106], activated charcoal [107], zinc chloride [3,101,108], barium phosphate [101,107], or aluminium oxide [4]. Acrylates are formed from the methyl and ethyl esters of β-hydroxypropionic acid when these are distilled over alkali acetates [109], or heated in the gas phase over silica gel [110], or silicon dioxide saturated with concentrated sulphuric acid [111]. They can also be obtained in yields of up to 90% from the amide [112] and the nitrile [24,25,112–119] of β-hydroxypropionic acid.

Methyl acrylate is obtained in 50% yield from methyl β-methoxypropionate by passing the latter into concentrated sulphuric acid containing an inhibitor at 200°. [120] A similar process proceeds in the gas phase over catalysts [30,121–125]. Ethyl acrylate is obtained from ethyl β-ethoxypropionate [121,126–128]. Acrylates are formed from the esters of oxy-3,3′-dipropionic acid by the action of dilute sulphuric [129] or phosphoric [32] acid, or anhydrous zinc chloride [129] at an elevated temperature. When heated with sodium hydroxide [33], or 2-amino-, [35], or 4-methyl-2-aminopyridines [81], esters of β-aryloxy propionic acid give the corresponding monohydric and dihydric phenols. On being heated with anhydrous potassium carbonate at 100°, ethyl β-hydroxypropionate having the hydroxyl group esterified with *p*-toluenesulphonic acid decomposes almost quantitatively according to the following scheme [130]:

$$p\text{-}CH_3C_6H_4SO_2OCH_2CH_2COOC_2H_5 \rightarrow p\text{-}CH_3C_6H_4SO_2OH + CH_2{=}CHCOOC_2H_5.$$

Acrylates are also obtained from esters of β-acyloxypropionic acids [131–133].

The action of picric acid on ethyl β-hydroxy-β-(*p*-aminophenyl)propionate gives the picrate of *p*-aminocinnamic acid [134].

When esters of 2-carboxyethyl aryl sulphones are boiled with a 10% aqueous solution of sodium hydroxide, arylsulphinic acids are formed [60]:

$$ArSO_2CH_2CH_2COOR \rightarrow ArSO_2H.$$

It has been shown that a state of mobile equilibrium is established when ethyl acrylate reacts with ammonia [135]:

$$CH_2{=}CHCOOC_2H_5 \underset{-NH_3}{\overset{+NH_3}{\rightleftharpoons}} NH_2CH_2CH_2COOC_2H_5 \underset{+NH_3}{\overset{-NH_3}{\rightleftharpoons}}$$

$$\underset{+NH_3}{\overset{-NH_3}{\rightleftharpoons}} NH(CH_2CH_2COOC_2H_5)_2 \underset{+NH_3}{\overset{-NH_3}{\rightleftharpoons}} N(CH_2CH_2COOC_2H_5)_3.$$

Other investigators have also observed that, when ammonia and amines react with acrylates, a varied mixture of compounds is obtained [136,137]. Dry distillation of the ethyl ester of β-alanine leads to the formation of ethyl acrylate [138]. When ethyl β-(diethylamino)propionate is distilled, it slowly decomposes into diethylamine and ethyl acrylate [139]; its salts decompose more readily; for example, the hydriodide begins to decompose even at 100°, and at 165° this process is instantaneous [62].

When phthalic anhydride is heated with di-[2-(ethoxycarbonyl)ethyl]amine, *N*-[2-(ethoxycarbonyl)ethyl]phthalimide is formed in 75% yield [64]. Ethyl acrylate is formed by heating tri(ethoxycarbonyl)triethylamine [138,140,141], *N*-benzyl- and *N*-benzoyl-di(ethoxycarbonyl)diethylamines [140,141], or by treating ethyl (1-piperidyl)propionate with cyanogen bromide by Braun's method [142]. Oxidation of the addition product of ethyl acrylate and pyrazole gives pyrazole itself [143].

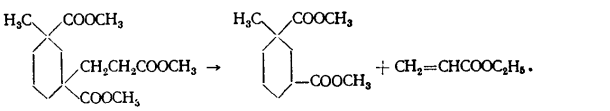
The preparation of an ester of β-(methylamino)-β-phenylpropionic acid is accompanied by the formation of the ester of cinnamic acid [144].

The decomposition products obtained by heating methyl β-(dimethylamino)propionate at 180–185° include acrylic acid. When the methiodide of this ester is heated with alkalis, it decomposes quantitatively into acrylic acid and trimethylamine [63]. When diesters of *NN*-di-(2-carboxyethyl)aryl sulphonamides are heated with 10% aqueous potassium hydroxide, they react according to the following scheme [70-62,92,93]:

$$ArSO_2N(CH_2CH_2COOR)_2 \rightarrow ArSO_2NHCH_2CH_2COOH.$$

The decomposition products obtained in the esterification of *NN*-di-(2-cyanoethyl)-α-amino-acids with hydrogen chloride in ethanol contain *N*-monocarboxyethyl derivatives and ethyl acrylate [145].

Other papers reporting the formation of acrylates from esters of β-substituted propionic acids have also been published [42,65,146-149]. In some reactions a carbon–carbon bond is broken [150,151], for example:



3. AMIDES OF β-SUBSTITUTED PROPIONIC ACIDS

Acrylamide is obtained in yields up to 80–96% from the amides of β-chloro-, [152] β-hydroxy-, [152] β-alkoxy-, [152,153] and β-(dialkylamino)-propionic acids [152,154]; it is also obtained by the following reaction [152,155]:

$$NH_4SO_3OCH_2CH_2CONH_2 \rightarrow CH_2{=}CHCONH_2 + NH_4HSO_4.$$

The $-CH_2CH_2CONH_2$ group, when located on the nitrogen atom of the pyrrole ring, is also eliminated under certain conditions [156]. Boiling of amides of β-aryloxypropionic acids [33] and amides of 2-carboxyethyl aryl sulphones [60] in aqueous sodium hydroxide gives the corresponding phenols and arylsulphinic acids:

$$ArOCH_2CH_2CONH_2 \rightarrow ArOH,$$
$$ArSO_2CH_2CH_2CONH_2 \rightarrow ArSO_2H.$$

The removal of the 2-carbamoylethyl group from esters of phosphoric acid has been studied [40,41,43].

NN-Disubstituted acrylamides are obtained from the corresponding amino-acid amides (but not anilides) by heating the latter to 180–220°, [136,137,154] for example:

$$(C_2H_5)_2NCH_2CH_2CON(C_2H_5)_2 \rightarrow (C_2H_5)_2NH + CH_2{=}CHCON(C_2H_5)_2.$$

The piperidide of β-piperidylpropionic acid cannot be separated, as it spontaneously decomposes with the formation of the piperidide of acrylic acid [136]:

$$2C_5H_{11}N + CH_2{=}CHCOOCH_3 \rightarrow C_5H_{10}N{-}CH_2CH_2CO{-}NC_5H_{10} \rightarrow$$
$$\rightarrow C_5H_{11}N + CH_2{=}CHCONC_5H_{10}.$$

It is noteworthy that when the diamides of *NN*-di-(2-carboxyethyl)aryl sulphonamides are heated with 10% aqueous sodium hydroxide solution, the corresponding monoacids are obtained in 60–76% yield, and not the expected diacids [70-72,92,93]:

$$ArSO_2N(CH_2CH_2CONH_2)_2 \rightarrow ArSO_2NHCH_2CH_2COOH.$$

When the diamide of *NN*-di-(2-carboxyethyl)benzenesulphonamide is heated with a 10% aqueous solutions of ammonia, *N*-(2-carboxyethyl)benzenesulphonamide is obtained in 70% yield; under these conditions, the *NN*-dicarboxyethyl derivative remains unchanged [70].

As Rodionov and Kiseleva [157] have shown, when *N*-benzoyl-β-phenyl-β-alanine is treated with acetic anhydride, cyclisation to the tetrahydropyrimidine derivative is accompanied by the formation of considerable amounts of benzamide and cinnamide:

$$C_6H_5CH(NHCOC_6H_5)CH_2CONH_2 \rightarrow C_6H_5CH{=}CHCONH_2 + C_6H_5CONH_2.$$

Cinnamic acid has been separated from the reaction mixture obtained by the action of acetic anhydride on the amide of *N*-ethoxycarbonyl-β-phenyl-β-alanine. Rodionov and Yavorskaya [144] have shown that, when β-phenyl-β-(*N*-benzoyl-*N*-methylamino)propionamide is heated with oxalic acid, the main reactior product is cinnamide. When *N* benzoyl-β-piperonyl-β-alanine is heated with thionyl chloride, followed by treatment with ammonia, β-piperonylacrylic acid is formed [158]. Under the same conditions, *N*-benzoyl-β-(1-naphthyl)-β-alanine gives β-(1-naphthyl)acrylamide [159]. Cyclisation of the amides of *N*-methoxycarbonyl-, *N*-acetyl-, and *N*-benzoyl-β-piperonyl-β-alanines gives β-piperonylacrylic acid in addition to the corresponding tetrahydropyrimidines [158]. The dehydrobromination of amides of β-substituted propionic acids has also been studied [160-162].

The pyrolysis of 2-carbamoylethyl hydrogen sulphate [155] and of β-alkoxypropionamides [163,164], leading respectively to the formation of acrylic acid and its nitrile, have been reported. The reaction of 2-carbamoylethyl hydrogen sulphate with alcohols gives the corresponding acrylates [165].

4. NITRILES OF β-SUBSTITUTED PROPIONIC ACIDS

Acrylonitrile is formed in 75–80% yield when β-halogenopropiononitriles are treated with ammonia [166], potassium carbonate [167], alkali hydroxides [168-171], sodium cyanide [172], tertiary aliphatic [166,168-171] and primary aromatic [166,173] amines, and also some heterocyclic bases [166,174]. One of the main methods of preparing acrylonitrile is the dehydration of β-hydroxypropiononitrile [175].

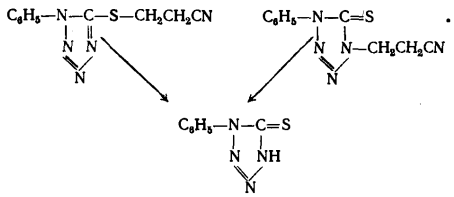
Decyanoethylation of β-alkoxypropiononitriles occurs when these compounds are subjected to reduction [176-180], hydrolysis [181-183], hydration [184] or pyrolysis [185], or when they are treated with organomagnesium compounds [186]. The same reaction occurs on reduction [187,188], hydrolysis [189], and pyrolysis [185] of bis-(2-cyanoethyl) ether, when it is heated in the presence of sodium formate [190] or with an aqueous solution of ammonia [183]. An attempt to cyclise the dicyanoethylation product of decan-1,10-diol to the corresponding iminonitrile by Ziegler's method was not successful, decan-1,10-diol being formed again in 90% yield [191]. When cleavage of the bond between the 2-cyanoethyl group and the oxygen atom occurred, the following were observed amongst the products of cyanoethylation: diethylene glycols [192]; poly(vinyl alcohol) [193,194]; some monosaccharides [195] and polysaccharides [196,197]; alicyclic [198], aromatic [178,199], and heterocyclic [200] alcohols; and phenols [35,36,81,176,185,201-207]. The product of the interaction of acrylonitrile with benzaldehyde in an alkaline medium eliminates acrylonitrile [208]. Other instances are also known of the breaking of the bond of the 2-cyanoethyl group with an oxygen atom in acid [185,209] and alkaline [175,187,209-214] media. Alkaline agents act as catalysts accelerating both the direct cyanoethylation of alcohols and the reverse reaction [215].

In the preparation of acrylonitrile from 2-hydroxypropiononitrile, the latter is sometimes esterified and the acrylonitrile is eliminated catalytically or thermally [175,216-222]. For example:

$$CH_3COOCH_2CH_2CN \rightarrow CH_3COOH + CH_2=CHCN,$$
$$p\text{-}CH_3C_6H_4SO_2OCH_2CH_2CN \rightarrow p\text{-}CH_3C_6H_4SO_3OH + CH_2=CHCN.$$

The removal of the 2-cyanoethyl group from phosphoric acid esters has been studied [40-43,223-245].

Decyanoethylation is observed when β-alkylthiopropiononitriles are hydrolysed by alkali [246], or when they are treated with organomagnesium compounds [247]; decyanoethylation also occurs when bis-2-cyanoethyl sulphide is reduced by Vyshnegradskiĭ's method [187]. Sulphones containing a cyanoethyl group are unstable in an alkaline medium and are readily decomposed by dilute alkali at room temperature to give acrylonitrile [60,248]. In the cyanoethylation of 1-phenyltetrazoline-5-thione, facile decyanoethylation of *S*- and *N*-isomers was observed [249]:



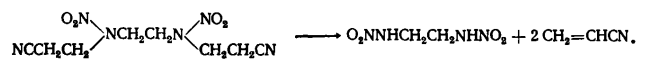
Many investigators [188,211,250-257] have studied the mobile equilibrium in the cyanoethylation of ammonia with acrylonitrile and have established the proportions of products of mono-, di-, and tri-cyanoethylation in relation to the reaction procedure and the proportions of the initial compounds. The products of this reaction undergo decyanoethylation on storage [250], when heated [211,252,258], on catalytic reduction [188,254], and when treated with ammonia [252,255,259]. Di-(2-cyanoethyl)-amine gives *N*-(2-cyanoethyl)acetamide [253] with acetic anhydride; with phthalic anhydride at 200° it gives cyanoethylated phthalimide [64]; and with perylene-3,4,9,10-tetracarboxylic acid at 230° it gives the dicyanoethylated di-imide of this acid [260,261]. When di-(2-cyanoethyl)amine reacts with chlorotriphenylmethane, a molecule of acrylonitrile is eliminated [262].

As is well known, hydrazine hydrate reacts vigorously with acrylonitrile, adding four molecules of the latter. However, when this product of the tetracyanoethylation of hydrazine is distilled under a high vacuum, it loses two molecules of acrylonitrile and is converted into a mixture of isomers of dicyanoethylated hydrazine [211]. Dibenzoyl-(2-cyanoethyl)hydrazine is formed by the action of benzoyl chloride on *unsym*-di-(2-cyanoethyl)hydrazine [263]. Kost and coworkers observed that, when (2-cyanoethyl)hydrazine is heated with mesityl oxide, 3,5,5-trimethylpyrazoline and acrylonitrile are formed [264]. It is known that *N*-cyanoethylated hydrazones undergo decyanoethylation in an alkaline medium [265], as do dicyanoethylated guanidines on cyclisation [266].

The decyanoethylation of some *N*-substituted β-aminopropiononitriles on distillation indicates the weakness of the bond between the cyanoethyl group and the nitrogen atom [250,254,267-270]. When the product of cyanoethylation of *N*-methyldodecylamine is heated for several hours at 250-275°, it decomposes almost quantitatively into the initial amine and acrylonitrile [271,272]:

$$CH_3(CH_2)_{11}N(CH_3)CH_2CH_2CN \rightarrow CH_3(CH_2)_{11}NHCH_3 + CH_2=CHCN.$$

When dicyanoethylated ethylenedinitramine is heated with aqueous alkali, the initial nitramine is formed in 82% yield [273]:



Decyanoethylation is observed when some β-alkylaminopropiononitriles are heated in the presence of water; it is also brought about by catalytic hydrogenation [275], by hydrolysis in an acid medium [276], and by other reactions [277,278].

On being heated, β-(diethylamino)propiononitrile decomposes into diethylammonium chloride and acrylonitrile [279,280]. Quaternary ammonium salts obtained from β-(dialkylamino)-propiononitriles smoothly eliminate acrylonitrile on pyrolysis [168,281]; in the presence of alkalis the reaction is rapid even at 100°. The yields of acrylonitrile and amines are as high as 90-95%. When the product of cyanoethylation of 2-amino-2-methylpropan-1-ol is alkylated with ethyl iodide, acrylonitrile separates [282]:

$$HOCH_2C(CH_3)_2NHCH_2CH_2CN + C_2H_5I \rightarrow HOCH_2C(CH_3)_2NHC_2H_5HI + CH_2=CHCN.$$

Methylation of β-(benzylamino)propiononitrile with a mixture of formaldehyde and formic acid gives *NN*-dimethylbenzylamine in 38% yield [283]:

$$C_6H_5CH_2NHCH_2CH_2CN + 2CH_2O + 2HCOOH \rightarrow$$
$$\rightarrow C_6H_5CH_2N(CH_3)_2 + CH_2=CHCN + 2CO_2 + 2H_2O.$$

Under the same conditions, the products of monocyanoethylation of tetramethylenediamine and hexamethylenediamine are converted into the corresponding tetramethyl derivatives of the diamines [284].

When the products of dicyanoethylation of a number of carboxylic acid amides are heated, especially in the presence of basic agents, *N*-monocyanoethylated amides are formed [35,64,70-72,81,92,93,250,285-293]:

$$RCON(CH_2CH_2CN)_2 \rightarrow RCONHCH_2CH_2CN + CH_2=CHCN,$$
$$RSO_2N(CH_2CH_2CN)_2 \rightarrow RSO_2NHCH_2CH_2CN + CH_2=CHCN.$$

Alkaline hydrolysis of *NN*-dicyanoethylated sulphonamides gives the corresponding *N*-monocarboxyethylated derivatives in yields up to 90%. [70-72,92,93,285,294-296]

$$RSO_2N(CH_2CH_2CN)_2 \rightarrow RSO_2NHCH_2CH_2COOH.$$

Under these conditions arylsulphonamides containing aryl and cyanoethyl groups at the nitrogen atom lose the cyanoethyl group [297]. Decyanoethylation may occur in the synthesis of *N*-cyanoethylated polyamides [298].

Recently, great attention has been paid to the decyanoethylation of the products of *N*-mono- and *NN*-di-cyanoethylation of amino-acids and their derivatives [35,81,145,205-207,250,278,299-313]. When two cyanoethyl groups are attached to a nitrogen atom, the first is removed more readily, and under milder conditions, than the second. By a suitable choice of reaction conditions, either one or two groups can be removed from the dicyanoethylation products. Some reactions of *N*-mono- and *NN*-di-cyanoethylated α-amino-acids, such as hydrolysis and cyclisation, are accompanied by decyanoethylation.

Some investigators [314] consider that the cyanoethyl group may be eliminated from dicyanoethylated aromatic amines, when these are cyclised. Decyanoethylation products have also been observed after the decomposition of β-arylaminopropiononitriles in acid or alkaline media [167,250,315-319].

Some derivatives of *N*-(2-cyanoethyl)pyrrole lose the cyanoethyl group when they are heated with sodium ethylate in absolute ethanol at 150°. When β-(5-ethoxycarbonyl-3--formyl-2,4-dimethylpyrrol-1-yl)propiononitrile is reduced by Kishner's method, 2,3,4-trimethylpyrrole is formed[156].

When heated in a vacuum to 250°, 1,3-di-(2-cyanoethyl)-indole eliminates acrylonitrile, giving a quantitative yield of 3-(2-cyanoethyl)indole, which is not decomposed by distillation in vacuum[73]. When heated with a concentrated solution of potassium hydroxide, *N*-(2-cyanoethyl)indole is hydrolysed to the corresponding acid; the decyanoethylation product, indole, is also formed in 10% yield. Under similar conditions, some derivatives of *N*-(2-cyanoethyl)-indole also give the corresponding indole derivatives[74,320]. Under certain conditions *N*-(2-cyanoethyl)indole can form indoline and acrylonitrile[321,322]. Heating of cyanoethylated benzimidazole with aqueous solutions of acids or alkalis leads to benzimidazole[80], and when 5-amino-1-(2-cyanoethyl)tetrazole is heated with aqueous barium hydroxide, 5-aminotetrazole is formed[323]. Pyrolysis of 1-(2-cyanoethyl)-6-methylpyrid-2-one gives 6-methylpyrid-2-one and acrylonitrile[324].

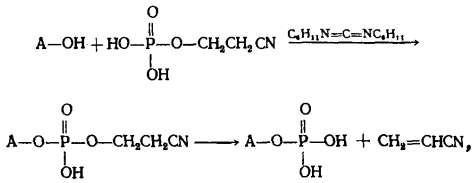
The cyanoethylation products of the following compounds have been decyanoethylated: pyrrolidine[325], derivatives of pyrazole[326,327], piperidine[251,278,325], morpholine[254], anabasine[328], phenothiazine[329,330], its benzo-derivative[331] and oxidation product[332], phenoxazine[331], phenoselenazine[333], tetrahydroharmine[334,335], 2-hydroxyquinoxaline[366], isocyanuric acid[337], dihydrobenzthiopyranoindole[339], and pteridine derivatives[339]. Attempts to remove the cyanoethyl group from 1-(2-cyanoethyl)-1,2,3,4-tetrahydro-4-ketoquinoline by means of bases have been unsuccessful. However, when this compound is treated with a mixture of concentrated hydrochloric acid and an excess of acetic anhydride, 1-acetyl-1,2,3,4-tetrahydro-4-ketoquinoline is obtained[314].

The bond between the 2-cyanoethyl group and the phosphorus atom has been studied in the mono-, di-, and tri-cyanoethylation products of phosphine, and also in their *P*-substituted derivatives. Although Rauhut and coworkers[340] were unable to remove the cyanoethyl group from the compounds mentioned above, other workers[341-344] have shown that *P*-cyanoethylated compounds can be decyanoethylated.

Halides of tri(2-cyanoethyl)tin are obtained by the action of halogens on tetra-(2-cyanoethyl)tin; under certain conditions the nitrile group is hydrolysed and two cyanoethyl groups are eliminated[345].

If a carbon–carbon bond is formed in cyanoethylation, it is usually very difficult to remove the 2-cyanoethyl group[250,346-348]. Under certain conditions, succinic acid dinitrile (the product of cyanoethylation of hydrocyanic acid) decomposes into hydrocyanic acid and acrylonitrile[211,349-351], the latter being obtained in up to 94% yield. Alkaline hydrolysis of tricyanoethylated nitromethane gives γ-ketopimelic acid, and a molecule of acrylonitrile is eliminated[211]. Some *C*-cyanoethylated compounds eliminate the cyanoethyl group under the conditions of the Fischer reaction[352].

Because acrylonitrile is readily eliminated from β-substituted propiononitriles, the 2-cyanoethyl group can be used as a protective group. It was used in this way for the cross--linking of two pyrazole nuclei by means of a methylene bridge attached to the 4-positions of both rings[326,327]; it has also been used in the synthesis of secondary amines[271,272], peptides[353], and monoesters of phosphoric acid[245]. 2-Cyanoethyl phosphate has been widely used in the synthesis of phosphate esters[223-243]. When the diesters of phosphoric acid formed are treated with mild alkali (barium hydroxide or 3 *N* aqueous lithium hydroxide at 100° for 15 min), acrylonitrile is eliminated and the monoester is formed. This method of phosphorylation is used in the synthesis of a number of nucleotides:



where A is a nucleoside residue.

Attempts have been made to use acrylonitrile for blocking sulphydryl groups of proteins[306,354]. The reaction in which *NN*-dicyanoethylated products are decyanoethylated has been used as the basis of a method for synthesising some *N*-monocyanoethylated compounds that are difficult or impossible to obtain by direct cyanoethylation with acrylonitrile[71,92,93,250,301].

5. ALKYLATIONS WITH THE AID OF β-SUBSTITUTED PROPIONIC ACIDS AND THEIR DERIVATIVES

The readiness with which β-elimination occurs in the β-substituted propionic acid series suggests that many alkylations carried out with the aid of β-substituted propionic acids and their derivatives proceed through a stage in which unsaturated compounds — acrylic acid, its ester, amide, or nitrile — are formed. This has been confirmed by studies of the mechanism and kinetics of these reactions[167,168,171,173,213,279,280,318,319,355-357].

When β-(methylthio)propionic acid is treated with hydrochloric acid, it forms di-(2-carboxyethyl) sulphide and dimethyl sulphide[358]. Under similar conditions, the hydrolysis of the methyl esters of β-(methylthio)- and β-(ethylthio)-propionic acids proceeds in the same way[358,359]; methanethiol and ethanethiol can be obtained by alkaline hydrolysis of these esters. When ethyl β-(methylamino)-propionate is heated to 130–140°, *NN*-bis-(2-ethoxycarbonylethyl)methylamine is formed[360]:

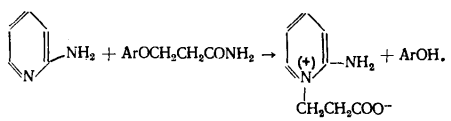
$$2\,CH_3NHCH_2CH_2COOC_2H_5 \rightarrow CH_3N(CH_2CH_2COOC_2H_5)_2 + CH_3NH_2.$$

When 2-carbamoylethyl hydrogen sulphate reacts with aliphatic and heterocyclic amines, carbamoylethylation of the amines takes place[155]. The amide of *N*-(2-carboxyethyl)-*p*-toluidine is formed when the following compounds are heated with *p*-toluidine in water at 100°; the amides of β-(alkylamino)- and β-aryloxy-propionic acids; the amides of *N*-mono-(2-carboxyethyl)-α-amino-acids and the diamides of *NN*-di-(2-carboxyethyl)-α-amino-acids; analogous derivatives of β-alanine; and sulphones containing the 2-carbamoylethyl group[60,361-363].

$$p\text{-}CH_3C_6H_4NH_2 + RCH_2CH_2CONH_2 \rightarrow p\text{-}CH_3C_6H_4NHCH_2CH_2CONH_2 + RH.$$

The products that have been obtained by the reaction of 2-carbamoylethyl hydrogen sulphate with alcohols and

phenols include acrylic acid, β-alkoxy- and β-aryloxy--propionic acids and the esters of these [165]. β-Arylpropionamides react with α-amino- [35] and γ-methyl-α-amino--pyrimidines [81] according to the following scheme:



It is interesting that when the 2-cyanoethyl ether of 2-naphthol is heated in benzene in the presence of alkali, the 2-cyanoethyl group is transferred from the oxygen atom to a carbon atom and 1-(2-cyanoethyl)-2-naphthol is formed [202,364,365]. An analogous reaction occurs with doubly cyanoethylated resorcinol [202]. When 1-phenyltetrazoline--5-thione is cyanoethylated, the *S*-isomer is converted to the *N*-isomer [249]. Attempts to transfer the cyanoethyl group in the indole ring from the nitrogen to the β-position have not been successful [75].

When diethylene glycol [192], acetamide [211], arylsulphamides [70,72,92,93,366], α-amino-acids [304,307,311], and phenylacetonitrile [348] are heated with their dicyanoethylation products, the 2-cyanoethyl groups are redistributed, and monocyanoethylated derivatives are formed, for example:

$$ArSO_2NH_2 + ArSO_2N(CH_2CH_2CN)_2 \rightarrow 2\,ArSO_2NHCH_2CH_2CN,$$
$$C_6H_5CH_2CN + C_6H_5C(CN)(CH_2CH_2CN)_2 \rightarrow 2\,C_6H_5CH(CN)CH_2CH_2CN.$$

Acetophenone with its tricyanoethylated derivatives gives mono- and di-cyanoethylation products [348]. When *unsym*--di-(2-cyanoethyl)hydrazine is treated with phenylisocyanate, a certain amount of *sym*-di-(2-cyanoethyl)hydrazine derivative is formed [367].

The occurrence of mobile equilibrium and reversibility in cyanoethylations is particularly well exemplified by the reaction of acrylonitrile with alcohols [175,210-212,250,368]. When β-alkoxypropiononitriles are heated or set aside with aliphatic or aliphatic–aromatic alcohols in the presence of alkalis or alkoxides, transcyanoethylation occurs [213,250,369,370]:

$$ROCH_2CH_2CN + R'OH \rightarrow R'OCH_2CH_2CN + ROH.$$

β-Alkoxypropiononitriles behave in the same way under the conditions of Vyshnegradskii's reaction [187]. Some β-alkoxypropiononitriles are used as cyanoethylating agents [35,81,182 201,202,213,250,371-377]. Bis-(2-cyanoethyl) ether has been used for the cyanoethylation of hydrogen sulphide [378], thiols and thiophenols [379], ketones [380], and aromatic amines [201,374]. 2-Cyanoethyl esters have been used for the cyanoethylation of aliphatic amines [381], benzene [219,382], resorcinol (in the nucleus) [383], pyrrole [384], and piperidine [385]. Much work has been done on *N*-substituted β-aminopropiononitriles as agents for the cyanoethylation of alcohols [168,371], malonic ester [376], triethyl phosphite [386], dimedone [387], aliphatic [371] and aromatic [167,201,206,279,280,373,388-391] amines, indole [73], piperidine [371], 9,10-dihydrophenanthridine [392], morpholine [376], pyrazolines [393], and pyrazolones [394]. β-Halogeno- [250] and β-hydroxy-propiononitriles [250] are used as cyanoethylation agents, as are also some products of the cyanoethylation of nitrogen-containing heterocyclic bases [250,388].

With the exception of *C*-cyanoethylated compounds, other β-substituted propiononitriles (β-halogeno-, β-alkoxy-, β-aryloxy-, and β-alkylamino-propiononitriles, *S*-cyanoethylated compounds, *N*-mono- and *NN*-di-cyanoethylated amino-acids, *NN*-dicyanoethylated arylsulphamides, cyanoethylation products of peptides and proteins) react with aromatic amines in water at 100° to form decyanoethylation and transcyanoethylation products [70-72,90-93,167,201,202,205-207 213,250,279,280,302-304,318,319,335,355,356,373,374,388-391,395]:

$$XCH_2CH_2CN + ArNH_2 \rightarrow ArNHCH_2CH_2CN + XH,$$

where X = halogen, RO, ArO, RS, ArS, $ArSO_2$, RNH, $(R)_2N$, HOOCCH(R)NH, etc. The reaction of β-substituted propiononitriles with 2-amino- [35] and 4-methyl-2-amino-pyridines [81] has been studied.

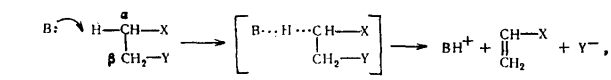
Products of the cyanoethylation of alcohols and aliphatic amines have been used instead of acrylonitrile in the reaction with phenylhydrazine for the synthesis of 3-amino-1--phenylpyrazoline [396]. The reaction of β-(dimethylamino)-propiononitrile with *p*-tolylhydrazine proceeds in the same way [397].

The use of β-substituted propiononitriles as cyanoethylating agents sometimes makes it possible to obtain cyanoethylated compounds when acrylonitrile cannot be used or when it gives low yields [250].

6. MECHANISM OF β-ELIMINATIONS

In most of the papers cited in this review, β-elimination was not the object of the investigation, but was only observed in studies on other problems. There are only a few papers in which some conclusions have been drawn as to possible reaction mechanisms or in which reaction kinetics have been studied [40,171,213,250,274,280,318,319,355-359]. These scattered data may be used, together with the general principles of the mechanisms of elimination reactions [398-401], to set up an approximate scheme of possible mechanisms for the reactions considered here.

The most important and the most widely studied class of β-elimination reactions in the β-substituted propionic acid series is that in which cleavage occurs under the action of basic agents. These reactions appear to proceed by a bimolecular elimination mechanism (*E*2) with an "*E*1 with B-like" transition state, in which rupture of the C–H bond precedes elimination of the β-substituent:

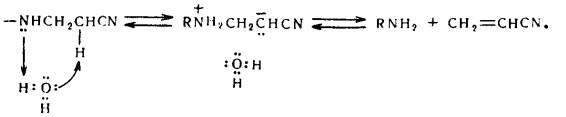


where X = COOH, COOR, $CONH_2$, CN; and Y = halogen, RO, ArO, AcO, H_2PO_3O, $(R)_2N$, $(R)_3N^+$, etc. However, it can happen that, under favourable conditions (low basicity of the agent B, low activating effect of the group X, and the presence in the β-position of substituents that facilitate rupture of the C–Y bond), there is a change to a synchronous or even *E*1-like bimolecular elimination mechanism [401].

The activating effect of the group X on the rate of elimination decreases in the order CN > $CONH_2$ > COOH, COOR. The particular ease with which decyanoethylation occurs in comparison with the removal of the 2-carboxyethyl, 2-carbamoylethyl, and 2-alkoxycarbonylethyl groups appears to be due to the high negative inductive effect (-*I*) of the nitrile group.

The scheme proposed by Bekhli [280] for the cleavage of β-dialkylaminopropiononitriles by a monomolecular mechanism (*E*1) does not appear to be valid. It was later shown that this reaction does not take place in the absence of basic agents [213]. It is also known that ammonium salts have little tendency to undergo cleavage by an *E*1 mechanism [401].

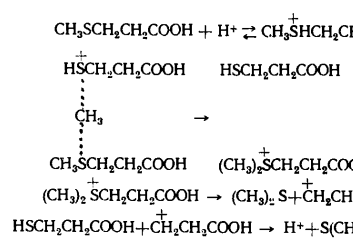
To explain the catalytic effect of water on the decyanoethylation of β-alkylaminopropiononitriles, a scheme has been proposed in which the water molecules act as a "proton carrier"[274]:



However, it is most probable that an $E2$ mechanism also operates here.

The scheme for nucleophilic bimolecular elimination does not appear to cover β-elimination reactions of β-hydroxy-, β-alkoxy-, β-aryloxy-, β-acyloxy-, and β-mercapto--propionic acids and their derivatives in an acid medium. The elimination may proceed through an oxonium ion. However, because of the lack of experimental results, it is not possible to advance a more detailed mechanism.

Challenger and coworkers have described a very interesting reaction of this type[358,359]. They observed that, when β-methylthiopropionic acid or its methyl ester is boiled with 6 N hydrochloric acid, extensive cleavage occurs with the formation of dimethyl sulphide and di-(2-carboxyethyl) sulphide. They propose the following mechanism for this reaction, which they have confirmed by numerous experimental results:



Up to now numerous pyrolytic cleavage reactions of β-halogeno-, β-hydroxy-, β-alkoxy, and β-acyloxy-propionic acids, and their esters, amides, and nitriles have not been studied at all. It may be supposed that they proceed by an "intramolecular elimination" (E_i) mechanism with a cyclic transition state, or by a radical mechanism similar to that of other pyrolytic eliminations[401]. However, cleavage of β-substituted propionic acids and their derivatives occurs at 150–250°, that is, at a temperature 100–200 deg lower than the temperature required for pyrolysis of the simplest alkyl halides, alcohols, and esters. This is probably due to the greater ease with which a hydrogen atom is eliminated from the propionic acids, arising from the effects of the carboxyl, ester, amide, and nitrile groups.

In conclusion it should be noted that at present it is still not possible to explain all the regularities and isolated anomalies of β-elimination. For example, the present review does not consider possible causes of the greater mobility of one 2-cyanoethyl group in the products of NN-dicyanoethylation, the effect of the β-substituent on ease of cleavage, isolated cases of carbon–carbon bond rupture, etc. More serious experimental work is required, with the use of physicochemical methods and kinetics studies, for the elucidation of the mechanism of β-elimination in the β-substituted propionic acid series.

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GIBBERELLINS

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II. Structure and chemical features of the gibberellins 851

III. Biogenesis of the gibberellins and their place among other natural polycyclic compounds 857

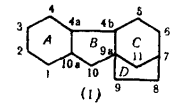
IV. Approach to an explanation of the mechanism of action of the gibberellins on higher plants 859

This review is devoted to the gibberellins — a new class of natural compound, the ever increasing interest in which is due to their high physiological activity as phytohormones.

The present article will be concerned with the chemical and biochemical aspects of the problem of the gibberellins. For a detailed analysis of the various physiological changes which can be observed in higher plants under the action of gibberellins, the reader is referred to several papers which have appeared in Soviet scientific literature [1-8].

I. GIBBERELLINS — NATURAL PHYTOHORMONES

The gibberellins, tetracyclic carboxylic acids, the structure of which is based on the hydrocarbon gibbane (I), were discovered by Japanese scientists investigating the reasons for the "bakanae" disease of rice ("foolish seedling disease"):



(I)

As long ago as 1898, Hori[9] established that the hypertrophic growth of the vegetative organs of rice seedlings which is typical of "bakanae" is caused by a fungus, the conidial stage of which was later named *Fusarium moniliforme* Sheld., the ascomycetous stage being named *Gibberella fujikuroi* Saw. In 1926, Kurosawa showed[10] that a similar physiological effect was produced by treating the seedlings with a culture medium of the fungus, free from mycelia, and in 1938 Yabuta and Sumiki[11] isolated as a crystalline material the active principles of the culture liquid of *Gibberella f.*, which they named gibberellin A and gibberellin B.

Subsequently the Japanese biochemists intensively studied the chemical structure and physiological properties of the preparations isolated, but their work only became known outside Japan in the 'fifties, when it gave an impetus to the development of studies in the field of gibberellins in other countries.

The first success in these investigations was the development of methods for the chromatographic purification of the crude preparation of gibberellin, which allowed Curtis and Cross[12] and also Stodola and coworkers[13] to isolate a pure substance with a high physiological activity, which was named gibberellic acid (GAc) or gibberellin A_3 (GA_3). The methods of fermentation and isolation which were developed out of Cross and Stodola's studies formed the basis of the industrial method of making GAc and made it an available substance[14,15]. Somewhat later, two other pure, physiologically active substances were isolated from the crude gibberellin preparation: gibberellins A_1[16-18] and A_2[17-19] (GA_1 and GA_2)†, and from the culture liquid of new strains of *Gibberella f.* the gibberellins A_4 (GA_4)[19-21], A_7 (GA_7)[22], A_9 (GA_9)[22], and A_{10} (GA_{10})[23] were obtained (see Table 1).

† The numbering of the first three gibberellins is determined by the order of their elution from columns during chromatography on a Celite 545 : Norite A mixture (1 : 1). The numbering of the other gibberellins (see below) was determined by the sequence in which they were isolated from natural sources.

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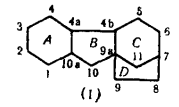

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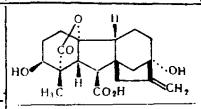
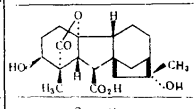
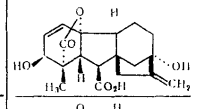
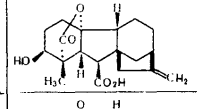
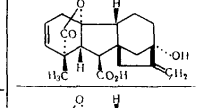
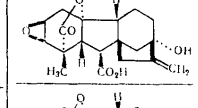
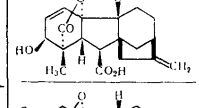
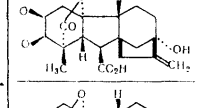
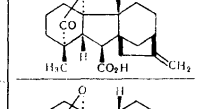
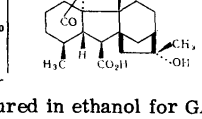
† The numbering of the first three gibberellins is determined by the order of their elution from columns during chromatography on a Celite 545 : Norite A mixture (1 : 1). The numbering of the other gibberellins (see below) was determined by the sequence in which they were isolated from natural sources.

TABLE 1. Physicochemical properties of the C_{19} gibberellins.

Name	Structural formula	M.p., °C	$[\alpha]_D$* (°C)	M.p. of methyl ester	$[\alpha]_D$ (°C) of methyl ester	pKa (25°) from Ref. 33	Ref.
Gibberellin A_1		255	+36 (20)	234	+46 (20)	3.97	16
Gibberellin A_2		235 255**	+11,7 (20)	190	+25 (26)	4.09	16,18,19
Gibberellin A_3 (gibberellic acid)		233	+92 (20)	209	+75 (20)	4.21	12,16
Gibberellin A_4		216 255**	−3 (20)	175	0±3 (20)	4.21	21
Gibberellin A_5		260	−77 (22)	191	—	4.09	30
Gibberellin A_6		206	−20 (26)	136	—	4.03	35
Gibberellin A_7		169 202**	+20 (24)	152 168**	+33 (23)	4.11	22
Gibberellin A_8		210	+13 (23)	221 231**	+14.8 (23)	4.04	35
Gibberellin A_9		208	−22 (22)	136	−15 (17)	4.26	22
Gibberellin A_{10}		245	+3	157	—	—	23

* Measured in ethanol for GA_1, GA_3, GA_7, and GA_9 and in methanol for GA_2, GA_5, GA_6, and GA_8.

** Polymorphic modifications.

The initial assignment of all these new substances to the gibberellin group was based on their common source in nature and the similarity of their spectra and physiological action on higher plants. Many investigations published in the 'fifties showed that the gibberellins are able to interfere actively in almost all the growth and development processes of plants. Thus, treatment with gibberellins stops the hibernation of seeds and stimulates their germination, accelerates the growth of seedlings, and "heals" the dwarf form of growth of dwarf mutants of higher plants. The last property is not possessed by any known chemical preparation. The ability of gibberellins to influence the photoperiodic reaction of flowering plants (long-day plants flower under short-day conditions after treatment with gibberellins) and their ability to alter the action of low temperatures (plants which need vernalisation flower normally and bear fruit without vernalisation after treatment with gibberellins) is extremely characteristic and specific.

Generalisation of the experimental results on the physiological activity of gibberellins led Chailakhyan[2,24] and, independently, Brian[25,26] to a hypothesis about the phytohormonal nature of the gibberellins. According to this hypothesis, the higher plants are capable of producing substances similar in properties to the gibberellins of fungal manufacture. These substances (endogenic gibberellins) play an important part in regulating the normal growth and the development of plants, and a shortage of them in the plant organism is responsible for the appearance of mutants with a dwarf form of growth, and also for the inability of plants which need vernalisation or a long day to develop normally in the absence of the appropriate external conditions.

Convincing confirmation of this hypothesis was given by recent investigations which showed that extracts of the epigeal parts of higher plants exhibit a gibberellin-like physiological activity and the substances present in them are almost indistinguishable from the fungal gibberellins in paper chromatography[4,27,28]. The chromatography of such extracts on a mixture of Celite 545 and Norite A permitted the separation — in addition to the known GA_1,[29-32] GA_3,[34,35] GA_4, and GA_7[23] — of three new individual substances: gibberellins A_5 (GA_5),[30,34] A_6 (GA_6),[35] and A_8 (GA_8)[35] (see also Table 1), the physiological activity of which is close to the activity of the fungal gibberellins‡.

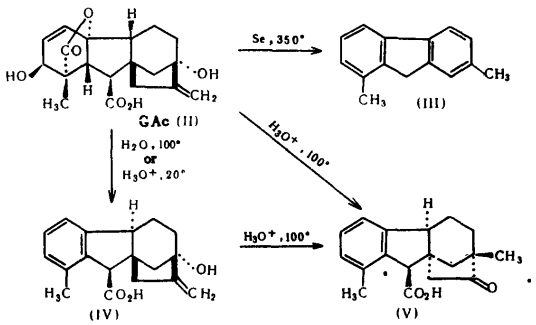
II. STRUCTURE AND CHEMICAL FEATURES OF THE GIBBERELLINS

In parallel with the work on the isolation of new gibberellins and study of the spectrum of their physiological activity, the investigation of the chemical structure of the compounds isolated was undertaken on a wide front. It was started by a group of Japanese chemists headed by Sumiki[41-46], who developed methods of degrading the gibberellins. However, up to 1955 these investigators worked with a preparation of gibberellin A, which was shown subsequently to be a mixture of GA_1, GA_2, and GA_3, therefore the characteristics which they obtained for the degradation products and also several conclusions about their structure needed checking. This task was completed by a group of English chemists headed by Cross, Grove, and McMillan, and as a result of their work the structure of the gibberellins which is now generally accepted was established and the peculiarities of the chemical conversions of this new class of natural compound were revealed.

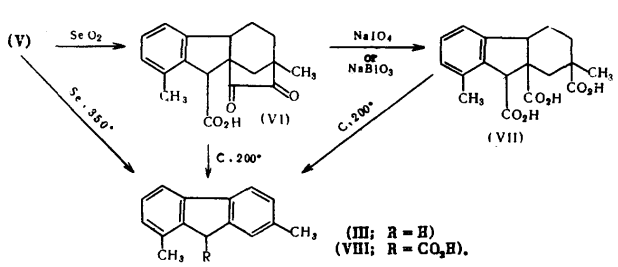
‡ Note that as well as the gibberellins substances more polar than the gibberellins and which exhibit gibberellin-like physiological activity were also separated chromatographically from the tissues of higher plants[36-40]. It was initially suggested that such substances are peptide complexes[36] or glucosides[37] of the known gibberellins and this received confirmation in the work of Sembdner and coworkers[38]. They showed that the highly polar neutral substance which they isolated from bean seeds is converted under acid hydrolysis conditions into a physiologically active organic acid comparable in polarity with known gibberellins. In addition to this acid, at least two other substances of carbohydrate type and three of peptide type were observed in the hydrolysate. Similar results were obtained by Sembdner and Schreiber[40] in studying tobacco seed gibberellins and also by Maksimov and coworkers in studying kale [*Brassica oleracea* var. *acephala* DC (Ed. of Translation)] gibberellins[36].

The key substance in the investigations to establish the structure of the gibberellins was GAc§, which is readily accessible. In this connection it is necessary to dwell in detail on the methods of determining the structure of GAc, particularly as the elucidation of the structure of this complex and very labile substance can serve as a good illustration of the enormous possibilities of contemporary organic chemistry and of the fruitfulness of a combination of chemical and physicochemical methods in studying natural products.

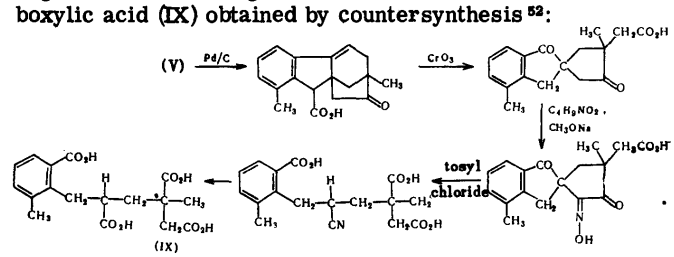
On the basis of the results of elemental and functional analyses, molecular weight determinations, and ultraviolet and infrared spectroscopic data, it was established that GAc has the empirical formula $C_{19}H_{22}O_6$, and is a tetracyclic, doubly-unsaturated dihydroxylactone-acid containing a methyl and a terminal methylene group[48]. It was shown that dehydrogenation of GAc with selenium at 350° [49] leads to 1,7-dimethylfluorene (III), which is evidence of the presence of the dimethylfluorene nucleus in its molecule. Subsequent stages of the work were connected with the revealing of the structure of the two main products of the degradation of GAc under acid conditions — allogibberic (IV) and gibberic (V) acids:



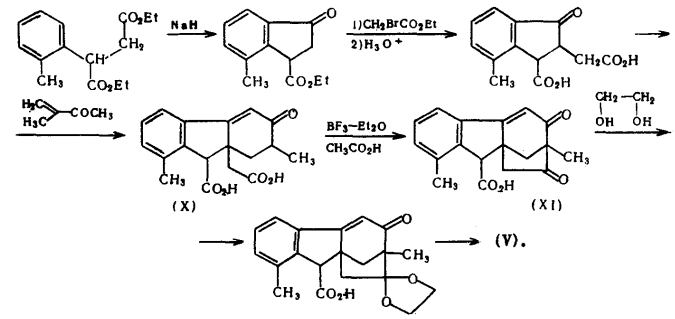
The analytical and spectroscopic data indicated that gibberic acid (V) is a tetracyclic dimethyl-substituted keto-acid of empirical formula $C_{18}H_{20}O_3$, in the skeleton of which there are an aromatic ring and a cyclopentane ring bearing a carbonyl group. The oxidation of gibberic acid with selenium dioxide leads to gibberdionic acid (VI) which under the action of sodium bismuthate or periodate is readily converted into a tricarboxylic acid (VII). The dehydrogenation of the latter, like the dehydrogenation of gibberic acid itself with selenium at 350°, leads to 1,7-dimethylfluorene (III):



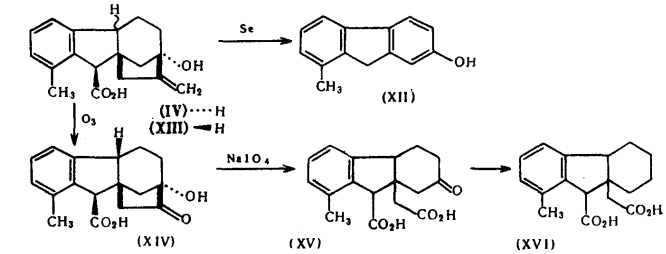
From these results it was concluded that the dehydrogenation of gibberic acid with selenium takes place without rearrangement of the skeleton and is accompanied by the breaking of the $-CH_2-CO-$ bridge connected to the flurorene nucleus at two quaternary carbon atoms. These facts, in conjunction with the formation of 1,7-dimethylfluorene-9-carboxylic acid (VIII) on the dehydrogenation of methyl gibberdionate, allowed gibberic acid to be given formula (V).[48,50] Its correctness was confirmed[51] by the oxidative degradation according to the scheme below to a tetracarboxylic acid (IX) obtained by countersynthesis[52]:



The final work in establishing the structure of gibberic acid was its synthesis, effected in 1960 by Loewenthal and Malhotra[53] by the scheme given below. The most interesting stage in this synthesis was the cyclisation (X) → (XI) in acetic acid in the presence of boron trifluoride–diethyl ether which enabled the tetracyclic diketo-acid (XI) to be obtained in ~ 80% yield:



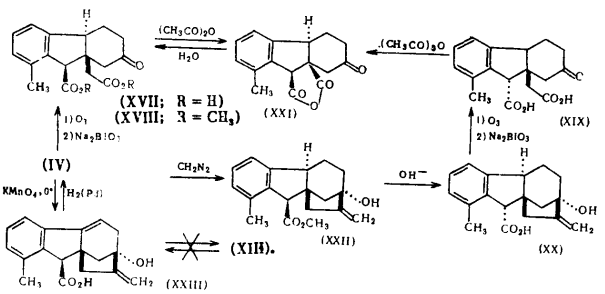
The other product of the degradation of GAc — allogibberic acid (IV) — is a tetracyclic carboxylic acid containing an aromatic ring, a tertiary hydroxyl group, and a terminal methylene group situated at the five-membered ring[48,50]. Since the dehydrogenation of allogibberic acid with selenium leads to 1-methylfluoren-7-ol (XII),[54] and when it is heated with dilute acids gibberic acid is formed (V), allogibberic acid was given formula (IV), and this was then confirmed by oxidative degradation as follows[52]:



As is seen from this scheme, the ozonation of epiallogibberic acid (XIII) — the epimer of (IV) at the $C_{(4b)}$ hydrogen atom — leads to the norketone (XIV) which in accordance with its α-ketol structure is readily cleaved by the action of sodium periodate or bismuthate. The reduction of the ketodicarboxylic acid (XV) thus obtained by the Kishner method leads to an acid (XVI), the structure of which was confirmed by countersynthesis[55,56]. A study of the stereochemistry of the conversions of the oxidative degradation products of allogibberic acid allowed its relative

§ In the fermentation of *Gibberella f.*, up to 1 g GAc,[47] 12 mg GA_1,[16] 0.3 mg GA_4,[21] 25 mg GA_7,[22] and 3–4 mg GA_9[22] are isolated from 1 litre of culture liquid. 2 mg GA_1,[28] 1 mg GA_5,[30] 8 mg GA_6,[35] and 16 mg GA_8[35] are isolated on extracting 1 kg of *Phaseolus multiflorus* seeds.

configuration to be found[57]. This problem was solved after the elucidation of the configuration of the carboxylic group at $C_{(10)}$ relative to the ethylene bridge at $C_{(7)}$–$C_{(9a)}$ and also the stereochemistry of the junction of rings *B* and *C*. The first part of the problem was solved by studying the formation of anhydrides by the dicarboxylic acids (XVII) and (XIX), which are epimeric at $C_{(10)}$ and were obtained in the oxidative degradation of allogibberic acid (IV) and its $C_{(10)}$ epimer (XX):



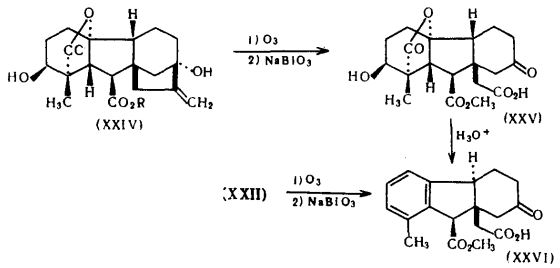
On heating with acetic anhydride, both isomeric acids give the same *cis*-anhydride (XXI), the saponification of which with water leads only to the *cis*-acid (XVII). Since this acid was identical with the degradation product of allogibberic acid (IV) the safe conclusion was drawn that in the latter there is a *cis* arrangement of the $C_{(10)}$ carboxyl group and the ethylene bridge.

The stereochemistry of the junction of the rings *B* and *C* was found by studying the stereochemistry of the hydrogenation of dehydroallogibberic acid (XXIII), formed on treating allogibberic acid (IV) with an aqueous solution of potassium permanganate at 0°. It is well known that in the catalytic hydrogenation of a double bond the addition of hydrogen proceeds from the least hindered side of the molecule. Therefore the formation of allogibberic acid (IV), uncontaminated with epiallogibberic acid (XIII) in the catalytic hydrogenation of acid (XXIII) indicated the *trans*-orientation of the hydrogen atom at $C_{(4b)}$ relative to the ethylene bridge and relative to the carboxyl group at $C_{(10)}$.

Analogous conversions in the gibberic acid (V) series showed that its carboxyl group is *trans*-oriented relative to the ethylene bridge and that rings *B*/*C* are *cis*-fused[41].

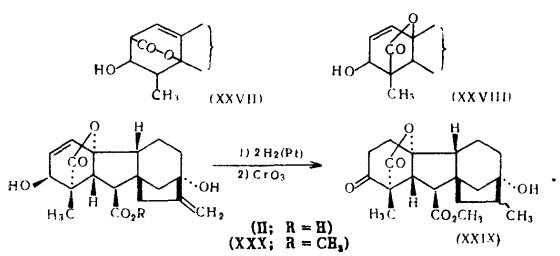
The examination of the chemical conversions still did not give the possibility of establishing the absolute configuration of gibberic and allogibberic acids. To solve this problem the method of optical rotatory dispersion was applied. With its aid Klyne[21,59], and independently of him Stork and Newman[58], showed that gibberic acid has the (7-*R*, 9a-*R*, 10-*R*)- and allogibberic acid the (7-*S*, 9a-*S*, 10-*R*)-configuration. However, this method did not allow the absolute configuration of the $C_{(4b)}$ asymmetric centre to be determined reliably, since it appeared that the rotatory dispersion curves of the compounds epimeric at $C_{(4b)}$ of this series are almost identical[59]. The problem was solved by using the method of circular dichroism, with the aid of which the (4b-*S*) absolute configuration of both acids was established[60].

The elucidation of the structure of gibberic and allogibberic acids allowed the next step to be taken in the proof of the structure of gibberellic acid — to introduce the hypothesis that the structure of rings *B*, *C*, and *D* in allogibberic and gibberellic acids is identical[61]. Confirmation of this was obtained by studying the oxidative degradation of the methyl ester of GA_1 (XXIV; R = CH_3) — the dihydro-derivative of the methyl ester of GAc. The ozonation of (XXIV) and the subsequent treatment of the resulting norketone with sodium bismuthate leads to the ester (XXV). On treatment with mineral acid the latter is converted into ester (XXVI) — the oxidative degradation product of methyl allogibberate (XXII)[61,62]:



The conclusion about the identity of the absolute configuration of rings *B*, *C*, and *D* in allogibberic and gibberellic acids, made in the same work on the basis of the optical rotatory dispersion results, seemed, however, inaccurate (see above). Use of the method of circular dichroism[60] showed that the absolute configurations of the centres $C_{(7)}$, $C_{(9)}$, and $C_{(10)}$ in these acids are identical but those of the $C_{(4b)}$ centre are contrary, that is, the system of rings *B*, *C*, and *D* in GAc has the (4b-*R*, 7-*S*, 9a-*S*, 10-*R*) absolute configuration.

The most complex step in determining the structure of GAc was elucidating the structure of ring *A*, for which in 1958 Japanese chemists proposed the partial formula (XXVII), [63] and English chemists formula (XXVIII) [64]:



Many conversions of GAc carried out by both groups of investigators showed that the (XXVIII) was the more probable formula. The final choice in its favour was made, however, only after employing the NMR method[65,66], which showed that GAc contains a hydrogen atom at $C_{(10a)}$ and four olefinic protons. Later, formula (XXVIII) was also confirmed by X-ray diffraction[60,67].

Many difficulties were encountered in proving the configuration of ring *A* of gibberellic acid. In 1959 Cross and coworkers[68] proposed formula (II) for GAc, in which the $C_{(2)}$ hydroxyl, which is readily epimerised by the action of 0.01 *N* alkali, was given the axial β configuration and the *A*/*B* ring junction was given the so-called *trans*-unnatural¶ (4a-α, 10a-β) configuration. The correctness of this formula was confirmed by nuclear magnetic resonance studies which showed the *trans*-fusion of the *A*/*B* rings in gibberellic acid. It was also demonstrated that ketone (XXIX) obtained by hydrogenation of the methyl ester of GAc (XXX) and subsequent oxidation of the OH group at $C_{(2)}$ exhibits a

¶ The name arises from the fact that most natural terpenes and steroids exhibit the antipodal fusion of rings *A* and *B*.

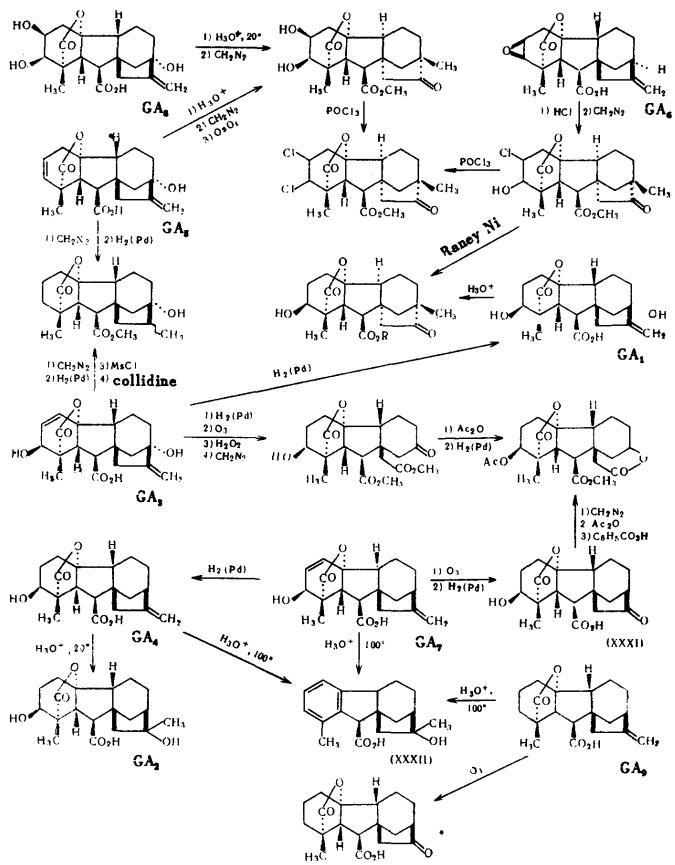
negative Cotton effect. This allowed, by application of the Octant Rule, a conclusion to be drawn about the β configuration of the hydrogen atom at $C_{(10a)}$.

In 1960 the Hudson–Klyne Lactone Rule[69] was applied to determine the stereochemistry of ring *A* of gibberellic acid; it enabled a decision to be made concerning the configuration of the lactone rings on the basis of the change in sign of the molecular rotation accompanying the opening of this ring. Stork and Newman[70] compared the changes in molecular rotation observable in the opening of steroid lactones with an α-configuration of the lactone ring on the one hand and of gibberellic acid on the other and concluded there was α-orientation of the lactone ring in GAc. Somewhat later Whalley and coworkers[71] investigated the regularities in the change in molecular rotation of lactones of the diterpene series with α- and β-configurations of the lactone ring and by applying the results obtained to the GAc system they concluded that a β-orientated lactone ring is present in ring *A* of GAc. However, this conclusion could not be considered to be firmly based as in both instances compounds with "natural" (that is, opposite to gibberellin) fused *A/B* rings were taken for comparison. The other chemical papers of 1960–1962 also did not give an unambiguous solution to the problem although detailed investigation of the stereochemistry of ring *A* made by Grove and coworkers[72] yielded a weighty argument in support of formula (II). Conclusive confirmation of it was obtained by X-ray diffraction[60] which demonstrated the α-orientated lactone ring in GAc.

Hence the structure of gibberellic acid is now reliably proved. It is expressed by formula (II) in complete agreement with which are the data obtained in studying the path of its biosynthesis.

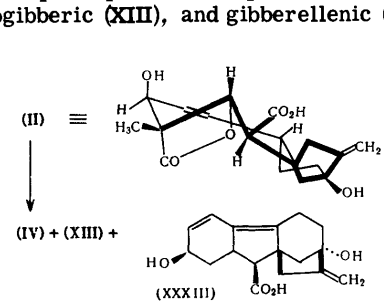
The structure of the other gibberellins† was found by referring them to the derivatives and degradation products of GAc.[19,21,22,30,35] It transpired that one group of gibberellins (GA_1, GA_5, GA_6, and GA_8) differ from GAc only in certain modifications of ring *A*. On treatment with hot solutions of mineral acids the gibberellins of this group are converted into gibberellic acid (V). The gibberellins of the other group (GA_2, GA_4, GA_7, and GA_9) differ from GAc more significantly. They do not contain a hydroxyl group at $C_{(7)}$ and thanks to this on ozonation they form norketones — for example, (XXXI) — which neither sodium bismuthate nor sodium iodate can cleave. Under the action of hot solutions of mineral acids the gibberellins of this group give aromatic acids — for example, (XXXII). The only change which occurs in the system of rings *C* and *D* during this treatment is the hydration of the terminal methylene group.

The chemical reactions which allow the structure of all the C_{19}-gibberellins at present known to be demonstrated are given schematically below:



During the elucidation of the structure of the gibberellins a series of chemical reactions was observed which are characteristic for these polycyclic compounds. We will consider the most interesting of them in detail.

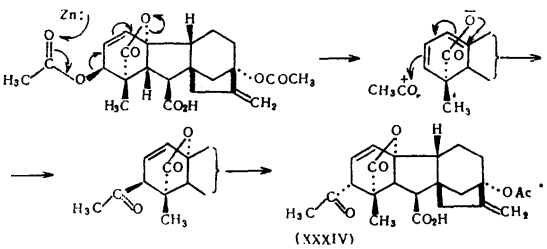
1. As mentioned above, gibberellins are extremely labile compounds, which undergo changes in aqueous solutions even at room temperatures. In this the most reactive centres of their molecules are the lactone ring, the $C_{(2)}$ hydroxyl group, and the $C_{(4b)}$ hydrogen. The opening of the lactone ring, which is accompanied by the formation of polyene and partly aromatised compounds, proceeds especially readily in gibberellins with a double bond in ring *A* (GA_3 and GA_7). In aqueous solutions it is observed even at room temperature. At elevated temperatures the process is complicated by epimerisation of the hydrogen atom at $C_{(4b)}$ and the principal reaction products are allogibberic (IV), epiallogibberic (XIII), and gibberellenic (XXXIII) acids:



The ease of formation of acids (IV) and (XXXIII) is due to the stereochemistry of the gibberellin molecules. According to the X-ray analyses[60], ring *C* of the gibberellins has a boat-shaped conformation, thanks to which there

† While this review was being prepared for publication Cross and Norton[108] isolated, from the culture liquid of *Gibberella f.*, a group of C_{20} di- and tri-carboxylic acids which are biogenetic precursors of the gibberellins. They proposed to name these compounds C_{20}-gibberellins. For more detailed information about these compounds see p. 858. The same authors reported[23,108] the isolation of a new C_{19} gibberellin, giberellin A_{11}; however, information concerning its structure and physicochemical properties has not been published yet.

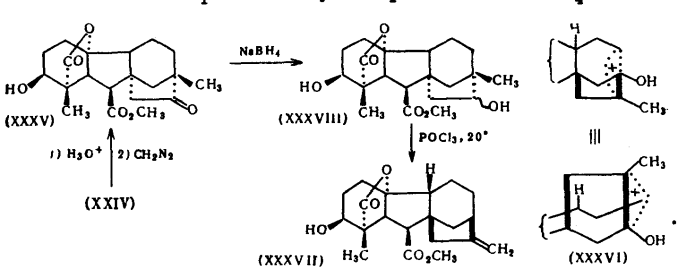
is considerable interaction of the spatially close axial hydrogen atom at $C_{(4b)}$ and carboxyl group at $C_{(10)}$ and with the ethylene bridge. Therefore the processes of epimerisation and dehydrogenation at $C_{(4b)}$, which remove this interaction, are energetically favourable. The instability of the lactone ring of gibberellins A_3 and A_7 is also due to steric reasons: the allyl lactone grouping formed by participation of the quaternary $C_{(4a)}$ atom is considerably strained and in consequence is readily opened under the influence of even such weak acids as the gibberellins themselves. The lability of the lactone ring of the gibberellins introduces several significant limitations into the chemistry of these compounds. For example, it is impossible to change from the compounds of the gibberellic acid series to the corresponding 7-deoxy-compounds with the aid of zinc and acetic acid anhydride. As McMillan and coworkers showed[73], under these conditions formation of an acetyl derivative (XXXIV) occurs, probably by the following mechanism:



2. Under conditions of catalytic hydrogenation under neutral and acid solvents the lactone ring of the gibberellins undergoes partial hydrogenolysis. The proportion of hydrogenolysis products in the reaction mixture is especially high for GA_3 and GA_7.[74-78]

3. The treatment of gibberellins containing a hydroxyl group at $C_{(7)}$ with hot dilute solutions of acids is accompanied — in addition to the opening of the lactone ring considered above and the epimerisation at $C_{(4b)}$ — by rearrangement of the carbon skeleton of rings *B*, *C*, and *D*, leading to gibberic acid (V).

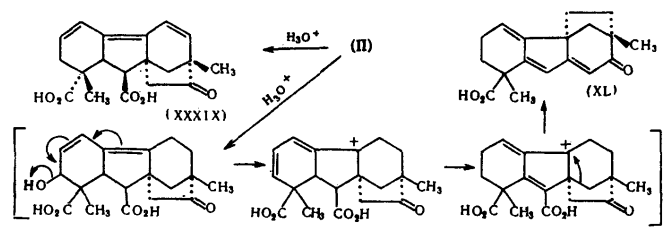
For gibberellins with a saturated ring *A* such a rearrangement takes place more readily than the opening of the lactone ring, so that it is possible to go, for example, from GA_1 (XXIV; R = H) to the ketone (XXXV). An analogous rearrangement is known for other natural compounds containing a fragment similar to rings *C* and *D* of the gibberellins (the diterpenes of the phyllocladene group, the diterpene alkaloids of the atisine group, etc.; see below). Its mechanism was studied in detail by Grove and Mulholland[57] and also by Birch and coworkers[79] who showed by the tracer method that a conversion analogous to the formation of (V) from GAc takes place by the mechanism of the Wagner–Meerwein rearrangement through a non-classical ion (XXXVI). This rearrangement of the gibberellin skeleton was used by Cross and coworkers[80] for going from derivatives of GA_1 to 7-deoxy-compounds of the GA_4 series:



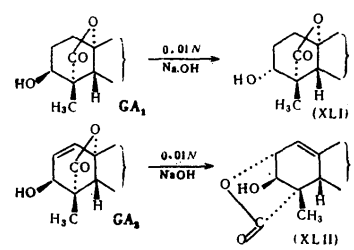
As the scheme shows, the methyl ester of GA_4 (XXXVII) was obtained by these investigators from the methyl ester of GA_1 (XXIV; R = CH_3) as the result of a double Wagner–Meerwein rearrangement: (XXIV) → (XXXV), (XXXVIII) → → (XXXVII). The low yield in this reaction is attributed to steric causes: on converting (XXXVIII) into (XXXVII) — in distinction from the conversion of (XXIV) into (XXXV) — the chair form of ring *C* becomes boat-shaped.

It is interesting to note that in gibberellins which do not contain a hydroxyl group at $C_{(7)}$ such a rearrangement is not observed. Under the conditions considered these compounds undergo only hydration of the terminal methylene group (see p. 854).

When gibberellins with an unsaturated ring *A* (GA_3, GA_7) are treated with an alcoholic solution of sulphuric acid, rearrangement of the carbon skeleton also occurs. However, unlike the reaction in an aqueous medium, the action of alcoholic sulphuric acid on these gibberellins is not accompanied by aromatisation of ring *A* and the main products of the reaction are the acids (XXXIX) and (XL)‡. A mechanism proposed for the formation of (XXXIX) includes a single, and that for the formation of (XL) a double, Wagner–Meerwein conversion[81] in accordance with the scheme:



4. Under weakly alkaline conditions the most "vulnerable" place of the gibberellins is again ring *A*. Treatment of the gibberellins possessing a saturated ring *A* (for example, GA_1) with 0.01 *N* NaOH is accompanied by epimerisation of the hydroxyl group at $C_{(2)}$ and leads to the lactone (XLI). Under similar conditions the gibberellins with an unsaturated ring *A* (GA_3 and GA_7) undergo an allyl rearrangement[82] and give lactones of type (XLII), which contain, like the original gibberellins, a hydroxyl group at $C_{(2)}$§:

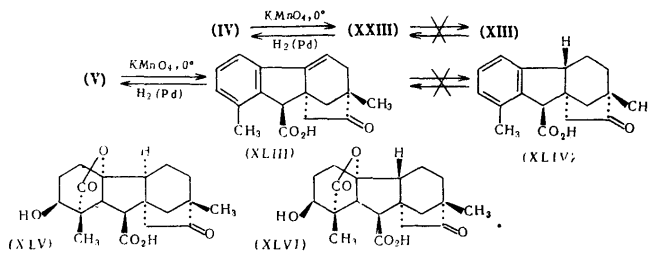


5. The complex stereochemistry of the gibberellins suggests that they should exhibit a variety of reactions of the free groups. As a rule, the information about such

‡ Note that the formation of (XXXIX) and (XL) is connected with the appearance of a dark red coloration accompanied by a blue fluorescence which is observed during the treatment of GA_3 and GA_7 with alcoholic solutions of sulphuric acid.

§ Note that epimerisation at $C_{(2)}$ and the conversion of (II) into (XLII) are accompanied by complete loss of physiological activity.

reactions is still very limited. As an example may be mentioned the difference in reactivity of compounds which are epimeric at $C_{(4b)}$, those studied in greatest detail being the degradation products of GAc containing an aromatic ring *A*.



Thus it has been found that allogibberic (IV) and gibberic (V) acids, for which the hydrogen atom at $C_{(4b)}$ has *trans*-orientation relative to the carboxyl group at $C_{(10)}$, are readily dehydrogenated under the action of potassium permanganate and even at 0° give the corresponding dehydro-acids (XXIII) and (XLIII). Contrary to this, the epimeric acids (XIII) and (XLIV), in which the hydrogen atom at $C_{(4b)}$ has *cis*-orientation relative to the carboxyl group at $C_{(10)}$, are stable to the action of potassium permanganate at 0° and do not form dehydro-acids (XXIII) and (XLIII) on hydrogenation.

The interaction of the carboxyl group at $C_{(10)}$ with the $C_{(4b)}$ hydrogen atom which is *cis*-oriented in relation to it is also apparent in the NMR spectra. Thus whereas in the spectrum of methyl gibberellate the signal of the proton at $C_{(4b)}$ is at $\tau = 7.7$, and in the norketone (XLV) it is at $\tau = 7.61$, in the norketone (XLVI) it occurs at $\tau = 7.2$.[59]

Yet another example of the sterically adjacent groups in the gibberellin molecule is provided by the interaction of the Δ^2 double bond and the carbonyl group of the lactone ring in GA_5 and its derivatives, which can be observed from the appearance of an anomalous absorption peak in the ultraviolet spectra of the corresponding compounds[30].

In examining the chemical features of the gibberellins it is impossible to avoid discussing the methods of analysing mixtures of these compounds of great structural similarity, particularly as these methods now form the basis for the identification of new gibberellin-like substances.

Although the first gibberellins were isolated as pure compounds by chromatography on columns packed with Celite 545 as long ago as the 'fifties, a reliable method of complete analysis of their mixtures did not exist until recently. The use of paper chromatography for this purpose allowed GA_8 and GA_9 to be determined reliably, but it was impossible to separate GA_1–GA_3 mixtures, or GA_4 and GA_7, by this method, although many chromatographic systems were tried[18,22,34,83,84]. Table 2 gives the R_f values of the gibberellins in the most convenient systems of solvents.

Satisfactory separation of a mixture of GA_1 and GA_3 was achieved by using centrifugal paper chromatography[85], and also thin-layer chromatography on aluminium oxide[85] and silica gel[86,87].

McMillan and Suter[88] made a complete analysis of a mixture of gibberellins by comparing the results of chromatography in a thin layer of silica gel G and kieselguhr G (see Table 3).

TABLE 2. Chromatography of gibberellins on Whatman No. 1 paper at 20°.[84]

Gibberellin	Value of R_f			
	system 1	system 2	system 3	system 4
GA_6	0.15	0.40	0.25	0.35
GA_3	0.29	0.50	0.40	0.48
GA_1	0.31	0.52	0.40	0.49
GA_4	0.33	0.51	0.42	0.51
GA_8	0.45	0.59	0.49	0.56
GA_4	0.60	0.72	0.57	0.72
GA_7	0.61	0.71	0.57	0.71
GA_9	0.725	0.77	0.65	0.78

* System 1: n-butanol–1.5 *N* ammonia (3 : 1); descending. System 2: propan-2-ol–water (4 : 1); ascending. System 3: n-butanol–t-pentanol–acetone–ammonia–water (5 : 5 : 5 : 2 : 3); descending. System 4: propan-2-ol–7 *N* ammonia (5 : 1); ascending.

TABLE 3. Thin-layer chromatography of the gibberellins.

Gibberellin	R_f*			
	on silica gel G		on kieselguhr G	
	system 1**	system 2	system 2**	system 3**
GA_6	0.04	0.00	0.28	0.06
GA_3	0.11	0.00	0.42	0.18
GA_1	0.11	0.00	0.54	0.26
GA_2	0.04	0.00	0.64	0.30
GA_5	0.25	0.21	0.95	0.76
GA_8	0.31	0.35	1.00	0.88
GA_7	0.37	0.70	1.00	1.00
GA_4	0.37	0.82	1.00	1.00
GA_9	0.75	1.00	1.00	1.00

* System 1: di-isopropyl ether–acetic acid (95 : 5). System 2: benzene–acetic acid–water (8 : 3 : 5). System 3: benzene–propionic acid–water (8 : 3 : 5).

** The upper phase of the system is used.

TABLE 4. Fluorescence of the gibberellins on thin-layer chromatograms.

Gibberellin	Colour of the fluorescing spot	Induction period of fluorescence, min	Gibberellin	Colour of the fluorescing spot	Induction period of fluorescence, min
GA_1	blue	30—40	GA_6	blue	10—20
GA_2	purple	4—8	GA_7	yellow	1—2
GA_3	blue-green	1—3	GA_8	blue	10—20
GA_4	purple	4—8	GA_9	purple	4—8
GA_5	blue	10—20			

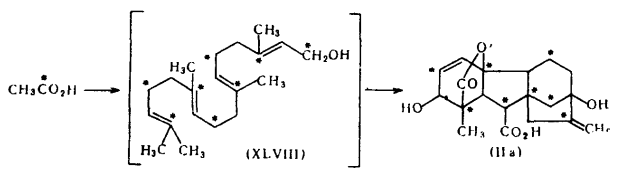
During thin-layer chromatography the gibberellins are observed by treatment of the plate with sulphuric acid and then heating. Spots which fluoresce in ultraviolet light appear, the colour and conditions of appearance of which (see Table 4) are important characteristics of the gibberellins[32].

This method allowed Jones and coworkers[31,32,87] to identify the known gibberellins in plant tissues at negligibly low concentrations (3–5 γ kg^{-1}).

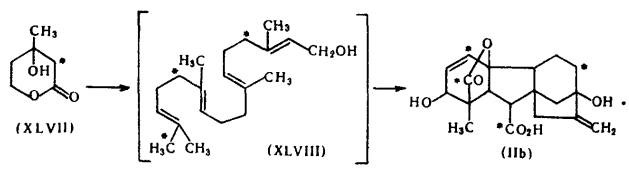
A rapid and reliable analysis of mixtures of the known gibberellins can be made also by gas–liquid chromatography[89]. Finally, very recently it was shown[90] that fragmentation mass spectrometry can be used for the analysis of mixtures and identification of individual gibberellins.

III. BIOGENESIS OF THE GIBBERELLINS AND THEIR PLACE AMONG OTHER NATURAL POLYCYCLIC COMPOUNDS

Even before the final elucidation of the structure of the gibberellins the study of the biosynthesis paths of GAc with the enzyme systems of *Gibberella fujikuroi* had begun. The first investigation of this problem was published by Birch and coworkers[91] who suggested that GAc is built by the fungus by the normal path of biosynthesis of cyclic diterpenes¶, that is, from molecules of acetic acid or the most characteristic precursor of the terpenes — mevalonolactone (XLVII). During this, the structural units are linked in accordance with the Ruzicka isoprene rule (by the head-to-tail principle), and the synthesis proceeds through a stage of formation of a normal acyclic precursor of the geranylgeraniol diterpenes (XLVIII). Cyclisation and slight transformation of the latter leads to GAc. This hypothesis could be easily checked by the use of labelled atoms. Actually, if it is true, then in GAc synthesised by fungi on a culture medium containing $^{14}CH_3CO_2H$, or mevalonolactone with ^{14}C in the $C_{(2)}$ position, the ^{14}C tracers should be distributed according to formulae (IIa) and (IIb):



(XLVIII) (IIa)

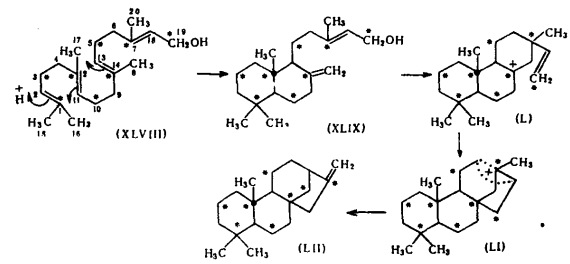


(XLVII) (XLVIII) (IIb)

Birch and his coworkers succeeded in showing that the tracer distribution corresponds strictly with the prediction.

Very recently[95], it was shown experimentally that the incubation of radioactive geranylgeraniol with *Gibberella f.* does not lead to the formation of radioactive gibberellic acid, and the precursor of the gibberellins is, as might have been expected, not this diterpene itself, but its pyrophosphate.

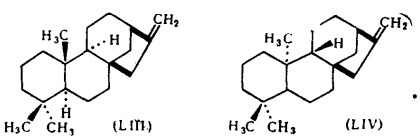
A detailed study of the reactions leading from the acyclic precursor of type (XLVIII) to GAc was not carried out in this work of Birch. However, it was assumed that the first stage in this conversion is the anti-*trans*-cyclisation at the Δ^{11} double bond to form a bicyclic product (XLIX) in which rings *A*/*B* are *trans*-fused. Subsequently there is the stage of dehydration of (XLIX) accompanied by closure of ring *C* and the formation of a carbonium ion (L), in which attack of the double bond by the cationic centre at $C_{(14)}$ passes through the stage of the non-classical ion (LI) to the tetracyclic precursor (LII):



(XLVIII) (XLIX) (L) (LII) (LI)

The first confirmation of this hypothesis was obtained even in the work of Birch and coworkers[91], since the distribution of the radioactive tracers in rings *C* and *D* of the gibberellic acid which is formed during fermentation in the presence of labelled acetic acid agreed well with the proposed scheme — compare formulae (LII) and (IIa).

Developing this hypothesis concerning the biogenesis of the gibberellins, Birch and Winter[96] suggested that the tetracyclic precursor of GAc of type (LII) is the well-studied diterpene phyllocladene (LIII).[97] However, their attempt to convert phyllocladene into GAc with the aid of the enzyme systems of *Gibberella f.* were unsuccessful: on incubation with phyllocladene labelled with ^{14}C, the fungus produced only non-radioactive GAc. In the light of contemporary ideas about the stereochemistry of the gibberellins this result does not seem unexpected, since phyllocladene exhibits the "natural" configuration at the fusion sites of rings *A* and *B*, contrary to the gibberellin configuration:



(LIII) (LIV)

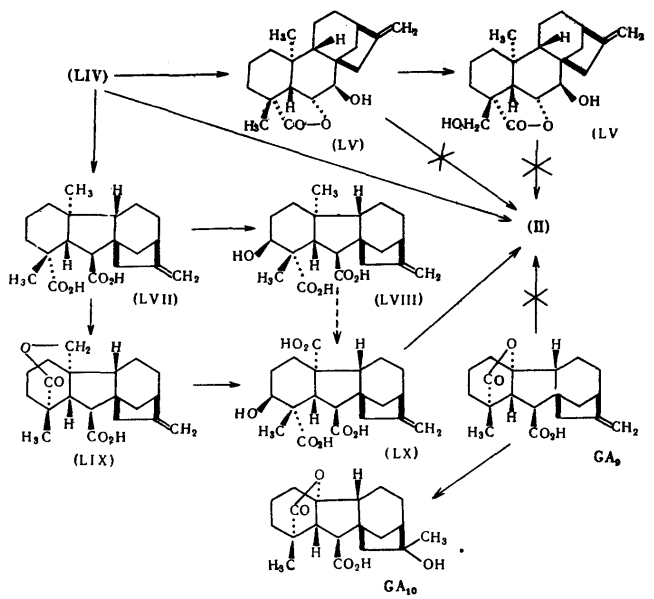
The true tetracyclic precursor of the gibberellins was found by Cross and coworkers[23,98] who showed that the culture liquid of *Gibberella f.* contains a tetracyclic diterpene (-)-kaurene (LIV),[99,100] which is easily converted into GAc under the action of fungal enzymic systems.

Extensive work carried out by the Cross group on the identification of the metabolites of various strains of *Gibberella f.* under different fermentation conditions[23,101–104] allowed the sequence of biosynthetic stages leading from kaurene to GAc to be noted. Until the publication of the results of these investigations it was thought[91,105] that the contraction of the six-membered ring *B* on going from the tetracyclic precursor to GAc precedes the introduction of the oxygen-containing functions into this ring. However, experimental verification showed[23] that neither hydroxykaurenolide (LV) nor dihydroxykaurenolide (LVI), which are isolated from the culture liquid of *Gibberella f.*, are converted by the fungus into GAc†.

¶ A discussion of the biosynthesis paths of the cyclic terpenes goes beyond the bounds of the present review. The reader should consult Refs. 92–94.

† GA_9 is also not a precursor of GAc. With the aid of the method of labelled atoms it was shown that under fermentation conditions GA_9 is converted into a new gibberellin, GA_{10}.[106]

Cross and his coworkers assume that the contraction of ring *B* is brought about in unoxidised kaurene, which is converted by acids (LVII)–(LX) into gibberellic acid:



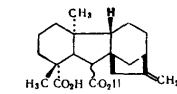
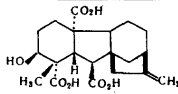
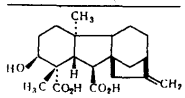
A detailed investigation of these last stages in the biosynthesis of GAc is now being made in Cross's laboratory. In the latest communications from this laboratory [107] the isolation of the acids (LVII)–(LX) from the *Gibberella f.* culture liquid has been described, and also the conversion of acid (LVII) labelled with ^{14}C at the $C_{(8)}$ methylene group into gibberellic acid (II) and the acid (LX). In both compounds the radioactive marker was found only in the terminal methylene group. On the basis of the results, Cross and Norton propose to call the acids (LVII), (LX), and (LVIII) — which are precursors of the gibberellins and exhibit gibberellin-like physiological activity — gibberellins A_{12}, A_{13}, and A_{14} respectively [108] (see Table 5). These compounds therefore disclose a new group of C_{20} gibberellins, which differ markedly from the C_{19} gibberellins considered above in the structure of ring *A*.

The investigation of the biosynthesis paths for the gibberellins in the tissues of higher plants has started only very recently. West and coworkers [95] have shown that in the incubation of a cell-fluid-free homogenate of endosperm nuclei of wild cucumber with [2-^{14}C]mevalonolactone, radioactive (-)-kaurene and (-)-kauren-19-ol are synthesised, which are converted by the enzymic systems of *Gibberella f.* into gibberellins. Hence it is quite probable that in plant tissues also the gibberellins are synthesised from (-)-kaurene.

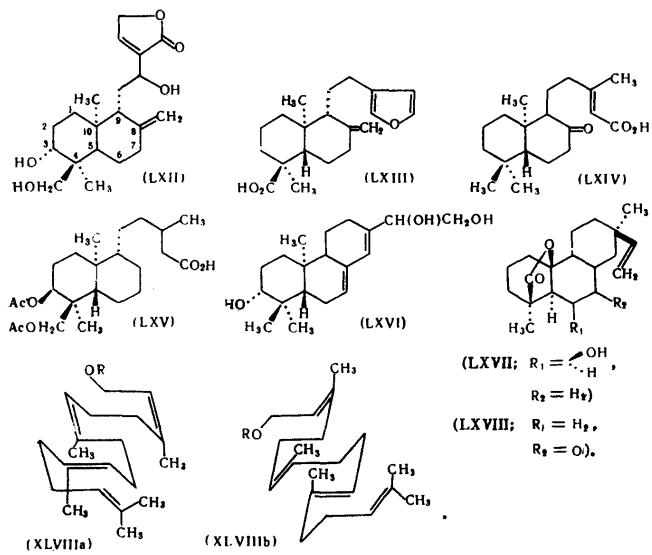
Some interesting work has been done by Lang and coworkers [109]. On incubating *Gibberella f.* with the diterpene steviol (LXI) these investigators detected the radioactive tracer in the mixture of gibberellins synthesised by the fungus. Careful chromatography of this mixture established that the tracer is concentrated in a zone free from known gibberellins but exhibiting high gibberellin-like activity.

A study of the biogenesis of the gibberellins allows us to understand the place of this unique polycyclic system among the natural compounds.

TABLE 5. Physicochemical properties of C_{20} gibberellins.

Name	Structural formula	M.p., °C	$[\alpha]_D$ (°C) n alcohol	M.p. of methyl ester, °C
Gibberellin A_{12}		245		liquid
Gibberellin A_{13}		194	—48(17)	117
Gibberellin A_{14}		232	—73	liquid

As is well known, geranylgeranyl pyrophosphate, an acyclic precursor of GAc, forms the start of a large group of natural diterpenes, which consequently are also the nearest biogenetic relatives of the gibberellins. When the cyclisation of geranylgeranyl pyrophosphate is interrupted at the stage of the GAc precursor of type (XLIX) (see p. 857), then bicyclic diterpenes are formed. In this, the transformation of the general precursor can mask the relationship of the compounds which are formed, leading to such different structures as andrographolide (LXII) [110], polyalthic (LXIII) [111], copalic (LXIV) [112], and eperuic (LXV) [113] acids‡.

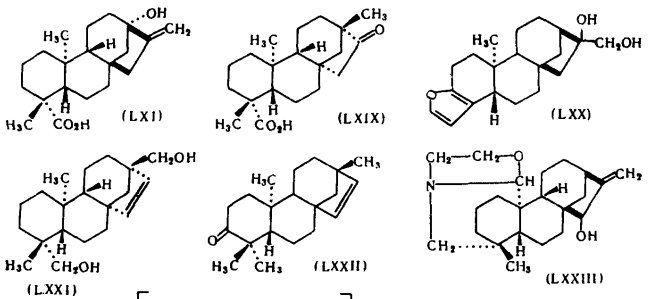


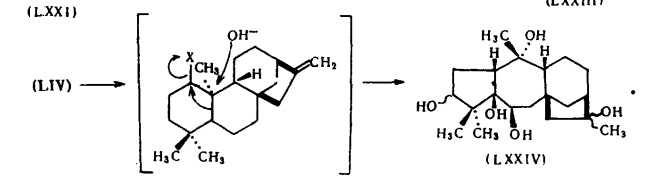
When the cyclisation of geranylgeranyl pyrophosphate is broken off at the stage of the precursor of type (L) then tricyclic diterpenes are formed. Further transformations of the precursor lead here to such substances as darutigenol (LXVI) [115], rosololactone (LXVII) [116], and rosenonolactone (LXVIII) [116,117]. Compounds (LXII)–(LXVI), like the gibberellins, possess an "unnatural" configuration of the *A/B* ring fusion and are formed, apparently, in the cyclisation of geranylgeranyl pyrophosphate in the same

‡ The configuration of these compounds at $C_{(8)}$ does not agree with the contemporary views on the stereochemistry of the diterpenes and requires verification [114]. The results of the verification have not yet been published.

"unnatural" conformation (XLVIIIa), which leads also to GAc. The lactones themselves (LXVII) and (LXVIII) have the 5α-, 10β-configuration§ usual for most terpenoids, and consequently are formed by cyclisation of geranylgeranyl pyrophosphate into conformation (XLVIIIc) antipodal to that which leads to the gibberellins. Therefore, despite the generality of the structural elements of ring *A*, lactones (LXVII) and (LXVIII) are biogenetically further from the gibberellins than darutigenol or andrographolide.

The cyclisation of geranylgeranyl pyrophosphate can lead, finally, also to a tetracyclic precursor of type (LII), to give initially the diterpenes of the phyllocladene group and their simplest derivatives. Among those closest structurally to the gibberellins there are many compounds in which the stereochemistry of the fusion of the rings *A*, *B*, and *C* is identical with the stereochemistry of the corresponding centres in GAc. Such compounds include kaurene (LIV), steviol (LXI) [118], isosteviol (LXIX) [181], cafestol (LXX) [113], beyerol (LXXI) [119], and stachenone (LXXII) [120]:





The biosynthetic transformations of the tetracyclic diterpenes can lead also to such natural compounds as the alkaloids of the atisine group — compare, for example, garryfoline (LXXIII) [121] — and the grayanotoxins — compare, for example, grayanotoxin A (LXXIV) [122]. The last is of special interest as according to its structure it can be formed from the tetracyclic precursor of the gibberellins by rearrangement of the *A*/*B* ring system by a mechanism close to the mechanism for contraction of ring *B* in the gibberellins.

IV. APPROACH TO AN EXPLANATION OF THE MECHANISM OF ACTION OF THE GIBBERELLINS ON HIGHER PLANTS

The proof of the phytohormonal nature of the gibberellins and the detailed study of the spectrum of their physiological activity (see pp. 850, 851) led in turn to the problem of explaining the mechanism of action of the gibberellins on the higher plants.

Systematic investigations in this field started only seven or eight years ago and have proceeded in two main directions: (1) study of the effect of gibberellins on the exchange of substances and the activity of the enzymic systems; (2) study of the interaction of gibberellins with other plant growth regulators.

§ Steroid numbering.

Even in the first studies devoted to investigating the influence of gibberellins on the morphological features of plants it was shown that the operation of gibberellic acid is accompanied by an increase in the dry weight of the epigeal parts of plants with only slight change (sometimes even a decrease) in the weight of the roots. Hence the growth stimulation under the influence of GAc depends not only on an increase in the general assimilation but also a redistribution of the plant material to the benefit of the epigeal part [123]. Detailed study of the changes in the exchange of substances of the epigeal parts of plants brought about by GAc allowed observation of an intensification of the photochemical [1,123,124] and dark [124] fixation of carbon and also of the stimulation of the processes of water supply in plants [125], transpiration processes [125], and processes for the biosynthesis of protein and RNA [125-128]. A large volume of material has been published about the effect of GAc on the biosynthesis of chlorophyll. As is well known, one of the distinctive features of plants treated with GAc is chlorosis However, a combination of treatment with GAc and a greater supply of mineral supplements prevents chlorosis [123]. From these results, and also from determinations of the percentage of chlorophyll in digitalis [129] and buckwheat [130] plants it followed that GAc does not suppress the biosynthesis of chlorophyll. This conclusion does not contradict the results on the reduction in the percentage of chlorophyll in the dry residue of lettuce [131], and pea [132] seedlings and also in the leaves of flowering plants [133], since when there is a sharp change in the weight of dry substance of plants under the influence of GAc it would be more correct to determine not the change in the percentage of chlorophyll in the dry residue but the change in its total quantity which can be made by the given organ of the plant.

However, the most characteristic feature of the change in materials exchange in plants under the action of GAc is the intensification of phosphorus–carbohydrate exchange. Studies by many investigators have shown that treatment with GAc brings about the utilisation of stored carbohydrates in the plants: the processes of phosphorolysis of starch and cellulose are intensified, and there is a significant increase in the level of monosaccharides [123,127,128,134-138]. The most active utilisation of stored substances under the influence of GAc occurs in germinating seeds. Detailed information on this process was obtained by studying the interaction of GAc with enzymic systems responsible for the splitting of the higher sugars. The principal objects of investigation were germinating barley seeds in which Hayashi and coworkers [139,140] observed as long ago as 1940 a sharp rise in activity of α-amylase. Subsequent work [141-146] confirmed this and also showed that, in addition to α-amylase, GAc is capable of activating other hydrolytic enzymes which participate in the splitting of starch and cellulose: diastase [147], β-amylase [141,146,148], cellulose [142], and phosphorylase [135].

In 1960 Paleg [149] showed experimentally that the activation of the α-amylase of barley grains under the influence of GAc is due to an intensification of the biosynthesis of this enzyme. Further investigation [150] established that GAc initiates the synthesis of α-amylase and the splitting of starch in seeds which have lost the ability to utilise the stored substances as a result of the removal of the germ or of γ irradiation. The results obtained enabled Paleg to develop a hypothesis that the apparatus for the control at the start of the hydrolytic processes in seeds and consequently at the start of germination is present in the germ and includes an endogenic gibberellin, which is an initiator of the biosynthesis of hydrolytic enzymes.

These studies of Paleg explained the first principles of the ability of gibberellins to interrupt the rest period of the seed and to stimulate its germination. Unfortunately, the problem of the nature of other aspects of the physiological activity of gibberellins is much less clear.

For example, despite many investigations, the problem of the mechanism of the acceleration of the growth of seedlings and the "healing" of the dwarf mutants of higher plants under the influence of gibberellins is still not solved. It has been shown reliably [1,8] that the enhanced growth after treatment with GAc stems from an increase in the cell elongation and an acceleration of their division, but the mechanism of the influence of GAc on each of these processes is not clear. To explain the action of gibberellins on the cell elongation several hypotheses have been propounded which explain the physiological activity of the gibberellins by including them in a scheme for the exchange of indolylacetic acid and other heteroauxins. The experimental basis for these hypotheses was the observation of many instances in which the level of the endogenic heteroauxins was raised [151-153] and the activity of indolylacetic acid oxidase was suppressed [154-156] after treatment of plants with gibberellins and also of the facts of the synergism of auxins and gibberellins [157-161] in their action on the plant. On the basis of these facts Galston and Warburg [162] suggested that the gibberellins are stimulators of the biosynthesis of polyphenols, which are capable of inhibiting indolylacetic acid oxidase, and consequently of raising the level of the endogenic heteroauxins in the plants. According to Galston and Warburg's hypothesis, a direct consequence of this is an intensification of cell elongation — a characteristic reaction of plants to auxins.

However, the above hypothesis is contradicted by many experimental results, including those of Kato [163] and of Brian and Hemming [164], who observed a marked difference in the reactions of the higher plants to gibberellins and heteroauxins (see Table 6).

Better agreement with the experimental results was shown by the hypothesis of Brian and Hemming [157], according to which the intensification of growth under the influence of GAc is explained by the ability of the gibberellins to suppress the biosynthesis of the polyphenolic inhibitors of the heteroauxins. Hence according to this hypothesis, just as with the Galston–Warburg hypothesis, the reason for the physiological activity of the gibberellins lay in an increase in the level of the endogenic heteroauxins, but the absence of the activity of the gibberellins in certain biosyntheses characteristic for heteroauxins was explained by the absence of the inhibitor for the auxins. However, this hypothesis also did not explain all the facts, particularly the ability of gibberellins to act in the dark and also to be cumulative in action on plants with superoptimal (inhibiting) quantities of heteroauxins.

TABLE 6. Main difference between heteroauxins and gibberellins.

Bio-test	Auxin	Gibberellin
Transport polar	+	−
Promote root initiation	+	−
Inhibit root elongation	+	−
Delay leaf abscission	+	−
Inhibit lateral buds	+	−
Induce callus formation	+	−
Promote growth of intact plants, especially of drawf mutants	−	+
Promote seed germination and breaking of dormacy	−	+
Substitute for vernalisation	−	+
Promote flowering in long-day plants under unfavourable light conditions	−	+

In recent years the main sense of the above hypotheses — the ability of the gibberellins to stimulate the biosynthesis of polyphenols — has been demonstrated experimentally by Netherlands chemists [165] by the example of ferulic, caffeic, and chlorogenic acids. However, they put forward quite another interpretation of the results obtained. Since ferulic acid can serve as the starting point for the biosynthesis of lignin, these investigators suggested, and then demonstrated by experiment, that gibberellins stimulate the biosynthesis of lignin. And since lignin plays the part of a material which strengthens the bond between cellulose fibres and gives the cell wall strength and elasticity, these investigators consider that the gibberellins play a part independent of the other growth regulators in the cell growth process: by stimulating the biosynthesis of lignin they are able to facilitate the densification of the cell walls and give them the optimal mechanical properties.

French investigators [166] also had a separate viewpoint about the action (independently of other hormones) of the gibberellins on plant growth, making clear the synergism of the auxins and gibberellins by their ability to combine with a single enzyme having two active centres, so that the adsorption of one hormone facilitates the adsorption of the other.

The stimulation of the biosynthesis of polyphenols under the influence of gibberellins can also be the key to understanding the action of these substances on the photoperiodic reaction of plants.

Actually, in recent investigations [167,168] there have been observations that the light regime has a considerable effect on the activity of oxidising enzymes taking part in the respiration processes of plants. It appeared that long-day conditions activate the so-called terminal oxidases which contain heavy metals and are capable of being poisoned by poisons of the potassium cyanide and sodium azide type (for example, polyphenoloxidase and ascorbinase), but short-day conditions activate residual respiration oxidases (including peroxidases). As it was also found reliably [167,168] that the activation of polyphenoloxidase in a long day is due to the improvement in the supply of this enzyme by polyphenols, it is easy to see that the ability of gibberellins to stimulate the biosynthesis of polyphenols can be the biochemical basis for their action on a long-day plant under short-day conditions.

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Summing up all the results of the investigations in the field of the chemistry and biochemistry of gibberellins which have been considered, something must be said about the future development of this field of bio-organic chemistry.

Whereas in the 'fifties the central task of the problem of the gibberellins was the establishment of the structure of this group of natural compounds and revealing the spectrum of their physiological activity, the centre of investigation has now shifted to the field of studies of the biogenesis of the gibberellins and the mechanism of their action on the plant. In this connection there is great interest in studying the metabolism of GAc in plants, and also the isolation and study of the structure of new endogenic growth regulators which exhibit gibberellin-like physiological activity, but differ in properties from the known gibberellins [38,169-172].

A considerable part in future investigations of the problem of gibberellins will evidently be played by work on the full synthesis of these compounds and their chemical conversions [173-176], since in this way it is possible to find not only the connection between structural and physiological activity in this group of compounds but also to observe new forms of biological activity of gibberellin-like substances.

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GLYCOSPHINGOLIPIDS: ESTABLISHMENT OF STRUCTURE, SYNTHESIS, BIOLOGICAL ROLE

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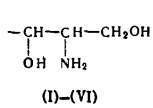
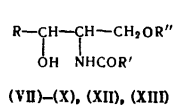
The present review considers lipids that are grouped together under the name glycosphingolipids. In addition to structural similarities, these compounds have at least one property in common in that they are capable of taking part in specific immunological reactions, the study of which may open a new approach to the understanding of the fine structural differences in animal and human tissues in normal and pathological states.

I. NOMENCLATURE

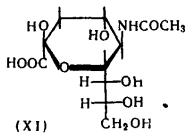
The term "sphingolipoids" was proposed by Carter to denote those lipids that contain the aliphatic amino-glycol sphingosine (I).[1] This term may now be extended to natural derivatives of dihydrosphingosine (II), C_{20}-sphingosine (III), and C_{20}-dihydrosphingosine (IV), which are found together with derivatives of sphingosine (I) in animal tissue, and also to the compounds phytosphingosine (V) and dehydrophytosphingosine (VI) and their C_{20}-homologues, which have been isolated from plants.



(I)–(VI)



(VII)–(X), (XII), (XIII)



(XI)

I, R = $CH_3[CH_2]_{12}CH{=}CH-$
II, R = $CH_3[CH_2]_{14}-$
III, R = $CH_3[CH_2]_{14}CH{=}CH-$
IV, R = $CH_3[CH_2]_{16}-$
V, R = $CH_3[CH_2]_{13}CH(OH)-$
VI, R = $CH_3[CH_2]_{11}CH{=}CHCH(OH)-$

VII, R′ = hexose
VIII, R′ = hexose–SO_3H
IX, R′ = oligosaccharide
X, R′ = oligosaccharide–hexosamine
XII, R′ = oligosaccharide–sialic acids
XIII, R′ = oligosaccharide–hexosamines–sialic acids
R as in compounds (I)–(VI)
R′ fatty acid residue

We shall apply the term "glycosphingolipids" to the group of sphingolipids that contain carbohydrates in addition to the sphingosines, (I)–(VI). In the present review we shall consider the glycosphingolipids of animal origin, that is, mainly derivatives of the sphingolipids (I)–(IV)† (Scheme 1).

The simplest representatives of this group, the cerebrosides (VIII), are monoglycosides of *N*-acetylsphingosines (ceramides).

The sulphatides or cerebroside sulphates (VIII) are sulphate esters of the cerebrosides.

The ceramide-oligohexosides (IX) are derivatives of the ceramides that contain oligosaccharides with simple hexoses as components. The name "cytosides" has also been proposed for ceramide disaccharides.

The globosides (X) are hetero-oligosaccharides of the ceramides containing hexosamines in addition to the simplest monoses; if the hetero-oligosaccharides contain sialic acids (XI) instead of hexosamines, they are termed "hematosides" (XII).

The sialic acids (XI) include all the acylated neuraminic acids[3], being, as it were, products of the aldol condensation of *N*-acylmannosamine and pyruvic acid.

The term "gangliosides" (XIII) is applied to derivatives of sphingosine containing fatty acids, monoses, hexosamines, and sialic acids.

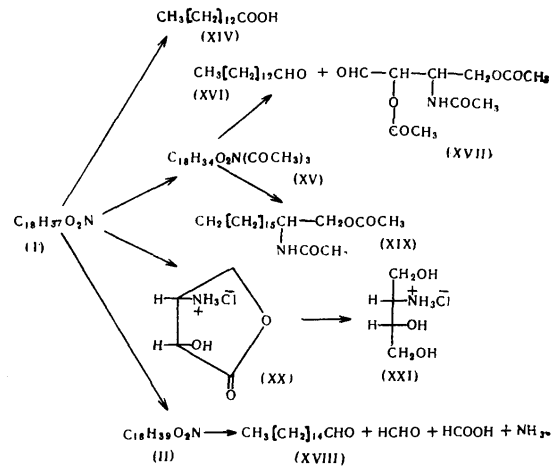
II. STRUCTURE AND DISTRIBUTION

1. Sphingosines

Sphingosine (I) was first isolated from brain lipids by Thudichum in 1901.[4] It was soon shown that it was an amino-diol with a double bond at the 4–5-position in a long hydrocarbon chain[5,6].

Oxidation of sphingosine (I) with chromic acid gave myristic acid (XIV),[7] and ozonolysis of triacetylsphingosine (XV) gave myristaldehyde (XVI) and a triacetylaminotetrose (XVII),[8] the structure of which was established by Cater[9,10] (Scheme 1)

Scheme 1



Two molecules of periodic acid are required for the oxidation of dihydrosphingosine (II) to palmitaldehyde (XVIII), formaldehyde, ammonia, and formic acid. When the triacetate (XV) was hydrogenated in the presence of platinum, the diacetate of 1-hydroxy-2-amino-octadecane (sphingine) (XIX) was formed as a result of hydrogenolysis of the 3-acetoxy-group, which indicates that one of the hydroxyl groups of sphingosine (I) is in the allyl position[11].

The D-configuration at the $C_{(2)}$ atom of sphingosine was established almost simultaneously by two methods. Carter and Humiston[11] made a comparative study of changes in optical rotation on dilution with water of dioxan or acetic acid solutions of *N*-benzoyl-α-aminostearic acid; the latter compound is isolated in the oxidation of *N*-benzoylsphingine, which is obtained from sphingosine triacetate (XV), and of *N*-acyl derivatives of known L- and D-amino-acids.

Kiss[12] converted sphingosine (I) by ozonisation into 3-amino-2-hydroxybutyrolactone hydrochloride (XX), which he then reduced to laevorotatory D-*erythro*-2-aminobutane-1,3,4-triol (XXI) (see Scheme 1).

The configuration at the $C_{(3)}$ atom was established by synthesis of the *threo*- and *erythro*-isomers of dihydrosphingosine (II)[13] (see pp. 868–869). The infrared spectrum of sphingosine (I) contains a band at 10.3 μm, indicating a *trans* double bond[14,15]. Total synthesis finally confirmed the structure of sphingosine (I) as D-(+)-*erythro*-*trans*-2-amino-1,3-dihydroxyoctadec-4-ene.

Dihydrosphingosine (II), which is identical with the hydrogenation product of sphingosine (I), was first discovered in the larvae of cat tapeworms[16], and it was soon also isolated[17,18] from the cerebroside fraction of the spinal cord and, in smaller amounts, from cow brain.

In recent years new amino-diols of animal origin, C_{20}-sphingosine (III) and C_{20}-dihydrosphingosine (IV), have been isolated. C_{20}-sphingosine (III) was first discovered by a group of Yugoslav biochemists in the brains of cows and horses[19,20]. The mixture of natural amino-diols was oxidised with chromic acid, and the methyl esters of the acids obtained were subjected to gas–liquid chromatography; it was shown that these contained methyl myristate and methyl palmitate, while methyl stearate was found in the products of oxidation and methylation of the dihydro-compounds. Recently, a rapid method was proposed for

† Recently Karlsson reported for the first time that derivatives of phytosphingosines (V) occur in animal and human tissues[2].

the determination of sphingolipid bases by gas–liquid chromatography of their trimethylsilyl derivatives[21].

The C_{20}-sphingosine (III), termed "icosisphingosine"[22], has also been found as the main component in a mixture of bases obtained by acid hydrolysis of a mucolipid[23,24] from ox brain and also of gangliosides from human brain[25].

Gas–liquid chromatography of a mixture of methyl esters of fatty acids obtained by periodate cleavage at the $C_{(2)}$–$C_{(3)}$ bond of the sphingosine fraction of human-brain gangliosides showed the presence of C_{20}-dihydrosphingosine (IV).[25] It was isolated by preparative paper chromatography of the mixture of dinitrophenyl derivatives of sphingosines obtained from human brain, cow brain, or human hair[26]. The ganglioside fraction of the brain consists of two-thirds C_{20}-sphingosines (III, IV) and one-third C_{18}-sphingosines (I, II) with about 10% of dihydro-compounds (II, IV).[27]

2. Cerebrosides

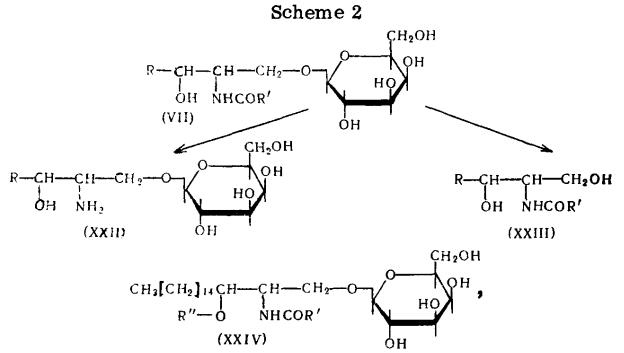
The first two cerebrosides — phrenosin and cerasine — were discovered by Thudichum in his study of the composition of the brain[28]. Later Klenk isolated two more cerebrosides, nervon and oxynervon[29,30]. These four cerebrosides differ from one another in their fatty acid components. Phrenosin contains cerebronic acid, $CH_3[CH_2]_{21}$–CHOH–COOH, cerasine contains lignocerinic acid, $CH_3[CH_2]_{22}COOH$, nervon contains nervonic (*cis*-tetracos-15-enoic) acid, and oxynervon contains hydroxynervonic acid. Cerebrosides containing other fatty acids are also known[31,32].

Repeated thin-layer chromatography has been used to separate a mixture of cerebrosides isolated from human spinal cords into 12 components containing different fatty acid residues[33]. Gas–liquid chromatography of the methyl esters of acids obtained by the hydrolytic cleavage of human brain cerebrosides indicates that these contain even-numbered and odd-numbered, saturated and unsaturated acids, as well as α-hydroxy-acids, with an unbranched chain and with from 14 to 26 carbon atoms[34].

The cerebrosides from normal human and animal brains contain galactose. In some anomalous conditions, in particular in lipidosis (Gaucher's disease), glucocerebroside accumulates in the human spleen[35,36]; it is also present, though in much smaller amounts, in the healthy human spleen[37].

The structure of cerebrosides has been established. When selectively hydrolysed, they are converted into sphingosine galactoside (psychosine) (XXII), and, under other conditions, into an *N*-acylsphingosine (ceramide) (XXIII)[28,29] (Scheme 2).

Scheme 2



where R = $CH_3[CH_2]_{12}CH{=}CH-$, R′ is a fatty acid residue, and R″ = $C_nH_{n+1}CH{=}CH-$.

Psychosine (XXII) is not reduced by the usual reagents for the aldehyde group; it is therefore a glycoside. Exhaustive methylation of cerebrosides (VII) and subsequent hydrolysis give 2,3,4,6-tetramethylgalactose, which indicates that these compounds contain a 1,5-pyranose ring[38,39].

When hexa-acetylphrenosin, or triacetylsphingosine (XV), is subjected to hydrogenolysis on platinum followed by hydrolysis, sphingine and acetic acid are formed[40], which means that the galactose is linked through the primary hydroxyl group of the ceramide. The β-configuration of the glycoside bond has been demonstrated by total stereospecific synthesis of some cerebrosides (see p. 872).

Using thin-layer chromatography on the cerebroside fraction of brain, Kochetkov and coworkers isolated a small quantity of a galactocerebroside with a greater R_f value than that of the classical cerebrosides[41]. The infrared spectrum and its behaviour on alkaline and acid hydrolysis indicated that this compound contains more than 90% of dihydrosphingosine, and that an alkenyl ether group is linked to the second hydroxyl group. The new compound was named sphingoplasmalogen (XXIV).[42]

3. Sulphatides

Thudichum detected sulphur in brain cerebrosides[28]. In 1933 Blix isolated the sulphatide (VIII) as the potassium salt from normal human brain (20–25% of total cerebrosides)[43]. The sulphatide contained fatty acids (mainly cerebronic), galactose, sphingosine, and a sulphuric acid residue. The sulphatides (VIII) can be separated from the cerebrosides (VII) by chromatography on diethylaminoethylcellulose[44].

Gas–liquid chromatography has shown that the composition of the sulphatides from grey and white matter of the human brain is similar to the fatty acid composition of the cerebrosides isolated from the same tissues, but the sulphatides contain smaller amounts of hydroxy-acids[45].

Yatzkewitz[46], using column chromatography on paper, separated sulphatides from human brain containing cerebronic, lignocerinic, and nervonic acids. Two sulphatides of rat brain isolated by Bakke and Cornatzer probably correspond to the sulphate esters of cerasine and phrenosin[47,48].

Thannhauser and Boncoddo[49], who methylated the cerebroside sulphate of cow brain and studied the products of subsequent hydrolysis by paper chromatography, showed that in this compound the sulpho-group is linked to the first hydroxyl group of galactose at $C_{(6)}$. However, re-investigation of the same sulphatide by exhaustive methylation in dimethylformamide, followed by methanolysis and gas–liquid chromatography of the methylated sugars, showed that methyl-2,4,6-trimethylgalactoside[50] was present, and not 2,3,4-trimethylgalactoside[49]. The absorption at 820 cm^{-1} (C–O–S vibrations) corresponds to the equatorial position of the $-OSO_3H$ group[51], which for the $C_{(1)}$ conformation of galactopyranose occurs when the $-OSO_3H$ group is in the 6-position or the 3-position. Obviously the sulphato-group is linked to the hydroxyl group at the $C_{(3)}$ atom of galactose, and Thannhauser and Boncoddo[49] were misled by the closeness of the R_f values obtained in the paper chromatography of the trimethylgalactoses.

On the basis of infrared spectra and a study of the methylation products, Hakomori and coworkers[52] confirmed the cerebroside 3′-sulphate structure; they also

isolated a complex sulphatide consisting of cerebroside 3′- and 6′-sulphates, which may be linked together as a diester of sulphuric acid.

4. Ceramide-Oligohexosides

Using chromatography on silicic acid of chloroform–methanol extracts, Rapport and coworkers[53] isolated the simplest ceramide-oligohexoside (IX) from human epidermal carcinoma, and they named it cytolipin H.[54,55] Compounds of similar structure have been separated from ox spleen[56,57], human spleen[37], horse erythrocytes[58], human erythrocytes[50], and human kidney tissue[59,60].

Cytolipin H is a mixture of ceramide β-lactosides in which sphingosine is linked by an amide bond with lignoceric [tetracosanoic], palmitic, behenic [docosanoic], or (to a lesser degree) another higher fatty acid[61]. The fatty acid composition of the compound was elucidated by paper chromatography and gas–liquid chromatography.

Analysis of the products of acid hydrolysis of cytolipin H with the aid of paper chromatography showed that the carbohydrate portion of the molecule contains glucose and galactose in equimolecular amounts. The configuration of the carbohydrate residue was established by an immunochemical method in which the reaction of cytolipin H with antibodies is inhibited by the addition of simple carbohydrates[54] (see p. 873). Total synthesis confirmed its structure (see p. 873) as a D-*erythro*-*N*-acylsphingosine 1-*O*-β-lactoside.

Other ceramide oligohexosides (IX), galactosyl-(1→4)--galactosylceramide and galactosyl-(1→4)-galactosyl--(1→4)-glucosylceramide[60], have been isolated from human spleens[37], kidneys[59], and erythrocytes[62], and from cow kidneys, cow's milk[63], and horse kidneys.

5. Globosides

It has been shown by a study of the products of moderate acid hydrolysis, oxidation with periodic acid, and exhaustive methylation in dimethylformamide that globoside, the main glycolipid of human erythrocytes[58,64], is *N*-acetylgalactosaminyl-(1→6)-galactosyl-(1→4)-galactosyl-(1→4)--glucosyl-(1→1)-*N*-lignocerylsphingosine.

A compound similar in structure to the globoside from erythrocytes has been isolated from human kidneys by Rapport and coworkers[66] and also by Makita and coworkers[67], and shown to be *N*-acetylgalactosaminyl)-(1→3)-galactosyl--(1→4)-galactosyl-(1→4)-glucosyl-(1→1)-ceramide[59]. Globosides have also been obtained by silica-gel fractionation of methanol–ether extracts of sheep and guinea-pig erythrocytes[62].

Recently a glycosphingolipid was isolated[68] from cancer tissue which appears to be formally a globoside, but which differs from known compounds of this type in that it has a high content of glucosamine (9–10%) and a fucose 6-desoxyhexoside (8.5–9.5%). The ratio glucose : galactose : fucose is 1 : 2.3 : 1.2. This is the main component of water-soluble glycolipids of human adenocarcinomate. Attempts to obtain the same globoside containing fucose from normal tissues were unsuccessful.

6. Hematosides

The hematoside *N*-acetylneuraminyl-(2→3)-galactosyl--(1→4)-glucosyl-(1→1)-*N*-acylsphingosine was isolated from the erythrocyte stroma of dogs, cats, and horses by Yamakawa and Suzsuki[69], and later by Klenk and Padberg[70]. Its sialic acid[71,72] is easily eliminated[73] by the action of a specific hydrolytic enzyme, neuraminidase (or sialidase), isolated from *Vibrio cholerae*.

A hematoside that probably contains two molecules of galactose and no glucose has been separated from human brain[74–76]. A more complex hematoside containing four molecules of neutral hexose and two molecules of sialic acids per molecule of ceramide has recently been isolated from hog brain[77].

7. Gangliosides

Gangliosides were first discovered in 1925 by Landsteiner and Levene[78] in extract of horse kidney, but it was not until 1942 that Klenk[79] isolated the relatively pure compound from the human cerebral cortex; it contains sphingosine, glucose, galactose, galactosamine, *N*-acetylneuraminic acid, and higher fatty acids (mainly stearic acid) in equimolecular proportions[80,81].

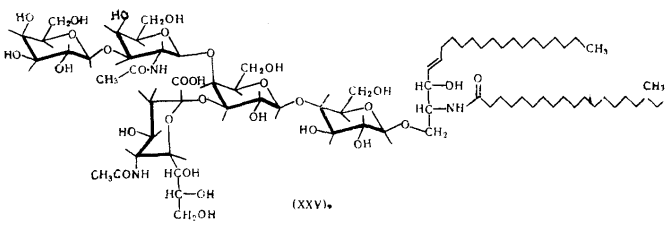
It was later shown that many gangliosides differing in composition and structure occur in nature. The fatty acid composition of brain gangliosides was studied by gas–liquid chromatography of the methyl esters obtained by saponification of the gangliosides[82–86]. Stearic acid was present to the extent of 72 to 96%; apart from this the other main acids in gangliosides are linear saturated C_{20}, C_{22}, and C_{24} acids.

The structure of the carbohydrate portion of the monosialoganglioside isolated from human brain (which in Svennerholm's nomenclature is denoted G_{M1}[87]) was determined by the collaborative work of several laboratories[88–91]. Moderate acid hydrolysis of G_{M1} gives the two disaccharides *O*-α-*N*-acetyl-D-galactosaminyl-(1→3)-galactose and *O*-β-D-galactopyranosyl-(1→3)-2-acetamido-2-desoxy-D--galactose[92].

On acetolysis with a mixture of acetic acid and acetic anhydride containing a little sulphuric acid[93], this ganglioside gives a ganglio-*N*-tetrose: galactosyl-(1→3)-*N*--acetylgalactosaminyl-(1→4)-galactosyl-(1→4)-glucose; two ganglio-*N*-trioses: galactosyl-(1→3)-*N*-acetylgalactosaminyl-(1→4)-galactose and *N*-acetylgalactosaminyl--(1→4)-galactosyl-(1→4)-glucose; two ganglio-*N*-bioses: galactosyl-(1→3)-*N*-acetylgalactosamine and *N*-acetylgalactosaminyl-(1→4)-galactose; and a lactose: galactosyl--(1→4)-glucose, the structure of which was established by periodate oxidation followed by reduction with potassium tetrahydroborate. The following saccharides containing *N*-acetylneuraminic acid were also isolated: sialyl-(2→3)--galactose, sialyl-(2→3)-galactosyl-(1→4)-glucose, sialylganglio-*N*-trioses, and a sialylganglio-*N*-tetrose. The structure of these compounds was determined by the enzyme method, which is based on the known relationship between the rate of enzymatic elimination of sialic acid and its location.

As has been shown by the periodate oxidation of methylsphingosine, obtained by exhaustive methylation of the ganglioside G_{M1}, the carbohydrate portion of this compound is linked through the primary hydroxyl group of sphingosine[88].

The structure of the ganglioside G_{M1} thus corresponds to formula (XXV); this structure was recently re-confirmed by periodate oxidation[94].



(XXV).

Another monosialoganglioside, G_{M2},[90] has also been isolated; normal human brain contains 3–5% of this compound, but much larger amounts are found in the brains of persons that have died of the infantile form of the hereditary "Tay-Sachs'" disease. For structure determination, the ganglioside G_{M2} was cleaved by acid hydrolysis to acylsphingosine saccharides and free sugars, which were then analysed quantitatively and characterised[90,95] (see Scheme 3).

Two disialogangliosides (G_{D1a} and G_{D1b}) and a trisialoganglioside (G_{T1a})[88,90,95,96] isolated from human brain are quantitatively cleaved by sialidase to give the monosialoganglioside G_{M1}. G_{D1a} is hydrolysed much more rapidly than G_{D1b}; G_{T1a} is first converted into G_{D1b} (with a little G_{D1a}), and then to G_{M1}. Hydrolysis of G_{T1a} with 0.01 *N* hydrochloric acid at 100° gives equal amounts of G_{D1a} and G_{D1b}. Since it is known that sialyl-(2→6)-lactose is hydrolysed more slowly by sialidase than sialyl-(2→3)-lactose, it may be supposed[95] that in G_{D1a} the second sialic acid molecule is linked with the $C_{(3)}$ atom of the end galactose, in G_{D1b} it is linked with the $C_{(6)}$ atom of the same galactose residue, and in G_{T1a} both hydroxyl groups are replaced.

Johnson and McCluer[94], using the method of periodate oxidation, studied the structure of yet another group of polysialogangliosides similar in structure to G_{M1} (see Scheme 3).

Oxidation of one galactose residue in the disialoganglioside G_{D1c} (according to Svennerholm's nomenclature; 3-G according to the present authors) shows that the end galactose residue is not replaced; destruction of only one molecule of *N*-acetylneuraminic acid and the stability of the second molecule indicate that the two sialic acid molecules are linked by a (2→8) bond[98–100]. Kuhn and Wiegandt isolated such a disialoganglioside[101].

The requirement of 6 moles of periodic acid for the complete oxidation of the trisialoganglioside G_{T1b}[94] is explained by the elimination of 2 moles of *N*-acetylneuraminic acid and 1 mole of galactose, and the formation of the disialoganglioside G_{D1c} as an intermediate under the action of sialidase shows that G_{T1b} also contains a (2→8)-sialic acid dimer. It can be shown by cleavage with 2 moles of periodic acid that the end galactose is not replaced, and the third mole of *N*-acetylneuraminic acid is not linked to this galactose (as in G_{D1a}), but possibly to the $C_{(6)}$ atom of *N*-acetylgalactosamine, but further evidence is needed to confirm this.

The trisialoganglioside G_{T1c}, isolated by Kuhn and Wiegandt[101] (G_{IV} according to the authors), differs in the position of the third *N*-acetylneuraminic acid residue. It is possible that the fourth sialic acid residue in $G_{Tet.1}$ (G_V according to Kuhn), which was isolated with G_{T1c}, is linked to the $C_{(6)}$ atom of the *N*-acetylgalactosamine in the same way as the third residue in G_{T1b} (see Scheme 3).

Scheme 3 *

G_{M1}–	gal[1→3]galNHAc[1→4]gal[1→4]glu[1→1]–R
G_{M2}–	galNHAc[1→4]gal[1→4]glu[1→1]–R [3 ↑ 2] NAcHa
G_{D1a}	NAcHa[2→3]gal[1→3]galNHAc[1→4]gal[1→4]glu[1→1]–R [3 ↑ 2] NAcHa
G_{D1b}	NAcHa[2→6]gal[1→3]galNHAc[1→4]gal[1→4]glu[1→1]–R [3 ↑ 2] NAcHa
G_{D1c}	gal[1→3]galNHAc[1→4]gal[1→4]glu[1→1]–R [3 ↑ 2] NAcHa[2→8]NAcHa
G_{T1a}	NAcHa[2→6]gal[1→3]galNHAc[1→4]gal[1→4]glu[1→1]–R [3 ↑ 2] [3 ↑ 2] NAcHa NAcHa
G_{T1b}	NAcHa [2 ↑ 6] gal[1→3]galNHAc[1→4]gal[1→4]glu[1→1]–R [3 ↑ 2] NAcHa[2→8]NAcHa
G_{T1c}	NAcHa[2→3]gal[1→3]galNHAc[1→4]gal[1→4]glu[1→1]–R [3 ↑ 2] NAcHa[2→8]NAcHa
$G_{Tet.1}$	NAcHa [2 ↑ 6] NAcHa[2→3]gal[1→3]galNHAc[1→4]gal[1→4]glu[1→1]–R [3 ↑ 2] NAcHa[2→8]NAcHa

* gal = galactose; galNHAc = *N*-acetylgalactosamine; glu = = glucose; NAcHa = *N*-acetylneuraminic acid; R = ceramide.

Recently preparative thin-layer chromatography has been used to separate brain gangliosides, and a mixture of trisialogangliosides was obtained in which the ratios hexose : ceramide and galactose : glucose were 3 : 1, which could correspond to a content of 25% of galactose ganglioside with no glucose in this mixture[102].

Kuhn and Wiegandt[103], using chromatography on kieselguhr, isolated a new ganglioside from erythrocytes and milk of long-horned cattle; this contains glucosamine instead of galactosamine and is readily cleaved by employing neuraminidase[103]. Examination of enzymatic and acid hydrolysis and by ozonisation[104] showed that it may be similar to the ganglioside isolated previously from erythrocyte stroma[105].

In a study of substances that determine blood-group specificity[106] (see p. 873), two gangliosides were separated that contain galactosamine, glucosamine, galactose, glucose, sialic acid, fucose, and sphingosine residues; they differ in fatty acid composition and show a sphingosine : glucose : : sialic acid ratio of 2 : 1 : 1.

The molecular weight of gangliosides varies between 1500 and 3000. However, in aqueous solutions they may form micelles [74] with an aggregate weight of 250 000; some workers [107] consider these to be high-molecular compounds in which hundreds of structural components of ordinary gangliosides are combined [108].

In an aqueous medium, the micelle must be oriented in such a way that the neuraminic acid residues are on its surface so as to be able to associate with water molecules, but the lipid part of the molecule is screened inside. According to Klenk and Gielen [74], in organic solutions the micelle must be, as it were, turned inside out, with the hydrophilic neuraminic acid residues concealed behind a barrier of sphingosine carbohydrate residues and fatty acids.

Howard and Burton [109] put forward the hypothesis of van der Waals interaction between the hydrophobic residues in the micelle. Thus, for example, sphingosine ganglioside No. 1 may be drawn into association with the fatty acid chain of ganglioside No. 2, the sphingosine of which will be associated with the fatty acid chain of ganglioside No. 3, and so on. This means that kinetic liberation of one hydrophobic chain need not lead to dissolution of the ganglioside molecule, since the other hydrophobic chain will still be "entrapped" in the micelle.

Non-ionic and non-covalent bonds of this kind may occur in such heterogeneous micelle-like structure as cell membranes and subcellular particles consisting of lipids and proteins.

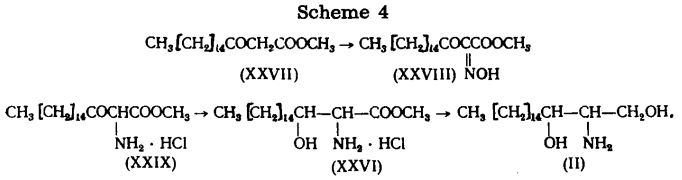
III. SYNTHETIC STUDIES

1. Synthesis of Dihydrosphingosine

Syntheses of sphingosine (I), dihydrosphingosine (II), and some sphingolipids, which have been carried out to finally establish the structure of these compounds, have advanced the development of biological studies, which require considerable quantities of the individual compounds.

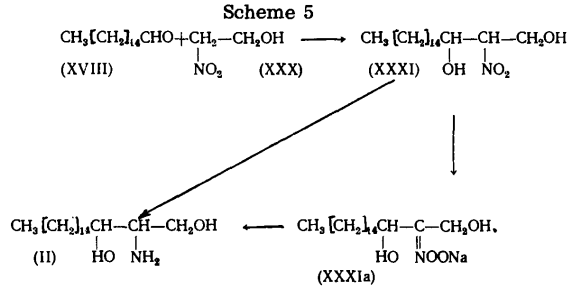
In 1947, Carter and coworkers [110] proposed a synthesis of dihydrosphingosine through methyl α-amino-β-hydroxystearate (**XXVI**), and in 1951 Gregory and Malkin [111] synthesised a mixture of racemates of dihydrosphingosine (II) from methyl 3-ketostearate (**XXVII**) by nitrosation [112] followed by stepwise reduction of the oxime (**XXVIII**), at first with palladium on charcoal in the presence of 2 moles of hydrochloric acid, then on platinum oxide, and finally with lithium tetrahydroaluminate (**XXVIII**) → (**XXIX**) → (**XXVI**) → → (II) (Scheme 4).

Scheme 4



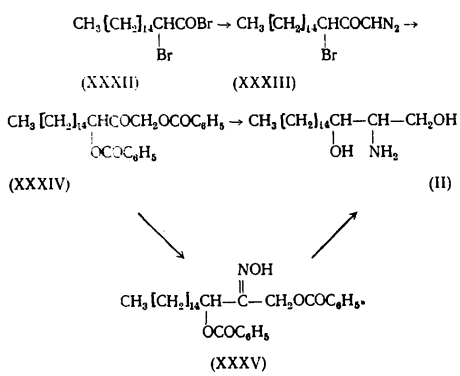
In the same year, Grob and coworkers [113] described a synthesis of a mixture of racemates of dihydrosphingosine (II): palmitaldehyde (**XVIII**) was condensed with nitroethanol (**XXX**) in the presence of sodium hydroxide, with subsequent reduction of the nitro-diol (**XXXI**) on Raney nickel (see Scheme 5); the *threo*-isomer (IIb) predominated in the mixture obtained. The total yield of dihydrosphingosine (IIa, b) was increased from 10.5 to 44% by using sodium methoxide as a condensing agent [114], separating the intermediate salt of the *aci*-form of the nitro-diol (**XXXIa**), and carrying out the reduction on platinum oxide.

Scheme 5



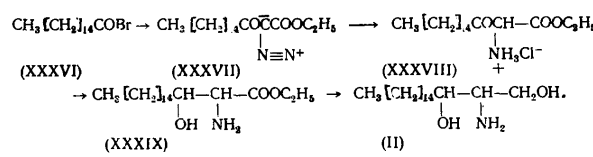
A group of Yugoslav investigators [115] has described a synthesis of a mixture of racemates of (II) in which 2-bromoheptadecanoyl bromide (**XXXII**) is condensed with diazomethane; the 3-bromo-1-diazodecan-2-one (**XXXIII**) is treated with silver benzoate and benzoic acid and the keto-diester (**XXXIV**) obtained is subjected to reductive amination on Raney nickel; alternatively, the oxime (**XXXV**), obtained from (**XXXIV**), is reduced with lithium tetrahydroaluminate (see Scheme 6).

Scheme 6



A synthesis of dihydrosphingosine (II) from the more accessible palmitic acid has also been described [116]: palmitoyl bromide (**XXXVI**) is condensed with diazoacetoacetic ester, and the 2-diazopalmitoylacetic ester (**XXXVII**) is reduced in steps, first by hydrogenation on palladium and then with sodium tetrahydroborate and lithium tetrahydroaluminate (**XXXVII**) → (**XXXVIII**) → (**XXXIX**) → (IIa, b) (see Scheme 7).

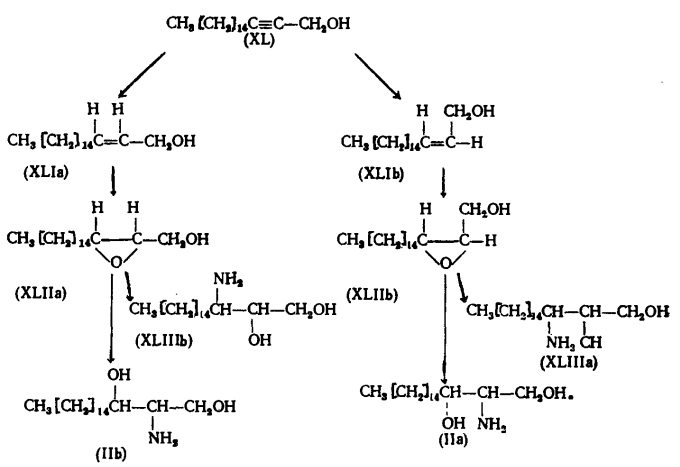
Scheme 7



A general defect of the syntheses described above is that they are not stereospecific; moreover, no methods of separating the diastereoisomers of (II) which are formed have been worked out.

The problem of the stereochemistry of sphingosine (I) at the carbon atoms $C_{(2)}$ and $C_{(3)}$ has been solved by stereospecific synthesis of the *erythro*- (IIa) and *threo*- (IIb) isomers of dihydrosphingosine [117,118]. Catalytic hydrogenation of 1-hydroxyoctadec-2-yne (XL) gives *cis*-1-hydroxyoctadecene (XLIa), but chemical reduction gives the *trans*-compound (XLIb); oxidation of the product with peroxyphthalic acid gives the corresponding *cis*- or *trans*-epoxide (XLIIa, b) Ring opening of the epoxides (XLII) with ammonia is accompanied by inversion of configuration and leads to *threo*- (IIb) and *erythro*- (IIa) dihydrosphingosines. Small quantities of the isomeric amino-diols (XLIIIa, b) are formed at the same time (see Scheme 8).

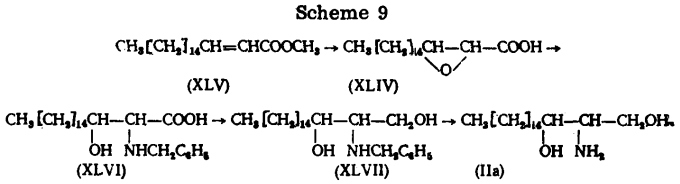
Scheme 8



At the same time, Carter and coworkers [13] synthesised D-(+)-, L-(-)-*erythro*, and DL-*threo*-dihydrosphingosines (IIa, b) by reduction of the corresponding *erythro*- and *threo*-α-amino-β-hydroxystearates [119] (XXVa, b) and separation of DL-*erythro*-dihydrosphingosine (IIa) into the antipodes as L-glutamates [120]. This work completed investivations to establish the structure of sphingosine (I).

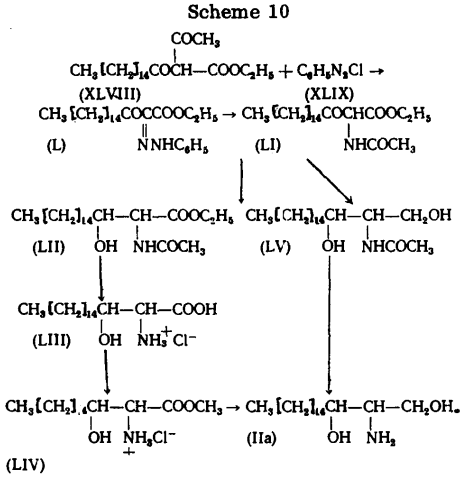
The great diversity of methods already proposed did not reduce the interest of chemists in developing new and more effective methods for the synthesis of dihydrosphingosine (II). Still another stereospecific synthesis of *erythro*-dihydrosphingosine (IIa) was described in 1964.[121] The reaction of *trans*-2,3-epoxystearic acid (XLIV), [122,123] obtained by epoxidation and subsequent saponification of methyl *trans*-octadec-2-enoate (XLV), with benzylamine leads to the formation of DL-*erythro*-2-benzylamino-3-hydroxystearic acid (XLVI). When the methyl ester (XLVI) was reduced with lithium tetrahydroaluminate and then hydrogenolysed, DL-*erythro*-dihydrosphingosine (IIa) was formed, (XLVI) → (XLVII) → (IIa) (see Scheme 9).

Scheme 9



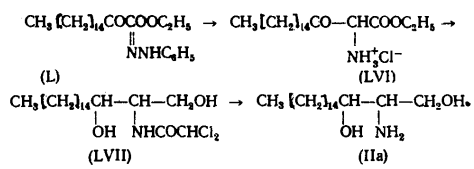
In developing a synthesis of sphingosine (see this page), Shapiro and coworkers also worked out a synthesis of (IIa). [124] Ethyl palimitoylacetoacetate (XLVIII) was condensed by Japp and Klingemann's method [125] with phenyldiazonium chloride (XLIX), and the product was hydrolysed to give the phenylhydrazone (L), which was then reduced with zinc and acetic acid in the presence of acetic anhydride to give ethyl 2-acetamido-3-ketostearate (LI). Reduction of (LI) with sodium tetrahydroborate gave an unseparable mixture of *erythro*- and *threo*-racemates (LII), which were converted into dihydrosphingosine (II) by saponification followed by esterification and reduction with lithium tetrahydroaluminate: (LII) → (LIII) → (LIV) → (IIa); the *erythro*-isomer of (II) was separated as the tribenzoate. It is more convenient to prepare (IIa) in two stages by reduction of (LI) with lithium tetrahydroaluminate to give *erythro*-*N*-acetyl-2-amino-1,3-dihydroxyoctadecane (LV), which is then hydrolysed (see Scheme 10).

Scheme 10



However, when the scale of the synthesis is increased, the yield of (IIa) decreases considerably because of the resistance of the amide (LV) to hydrolysis. For this reason, Shapiro and Sheradsky [126] later modified the method. Reduction of the phenylhydrazone (L) with zinc and aqueous 97% acetic acid leads to the keto-ester (LVI), which is separated as the hydrochloride. After this latter compound has been reduced with lithium tetrahydroaluminate, the mixture of isomers obtained is treated with methyl dichloroacetate [127], and *erythro*-*N*-dichloroacetyldihydrosphingosine (LVII) is separated; this is easily hydrolysed to *erythro*-dihydrosphingosine (IIa) (see Scheme 11). The second synthesis of dihydrosphingosine appears to be very efficient.

Scheme 11



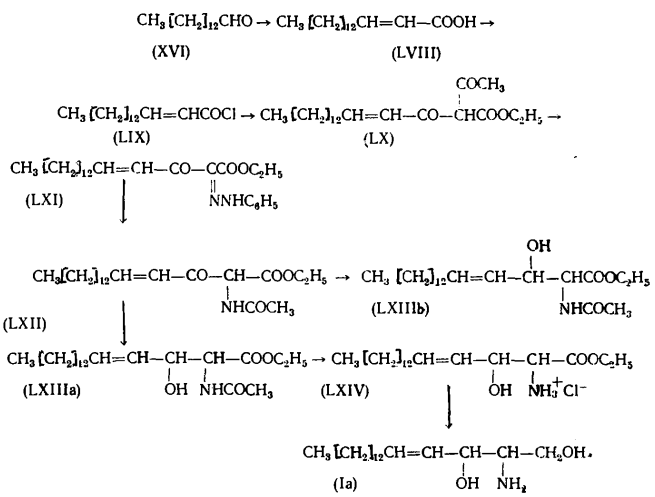
2. Synthesis of Sphingosine

There are two main schemes for the synthesis of sphingosine; these were first developed at almost the same time in the laboratories of Shapiro [128] and Grob [129].

In Shapiro's synthesis (Scheme 12), Knoevenagel–Doebner condensation of myristaldehyde (XVI) with malonic acid in the presence of piperidine gives *trans*-hexadec-2-enoic

acid (LVIII), from which the unstable *trans*-hexadec-2--enoyl chloride (LIX) is obtained by reaction with thionyl chloride.

Scheme 12



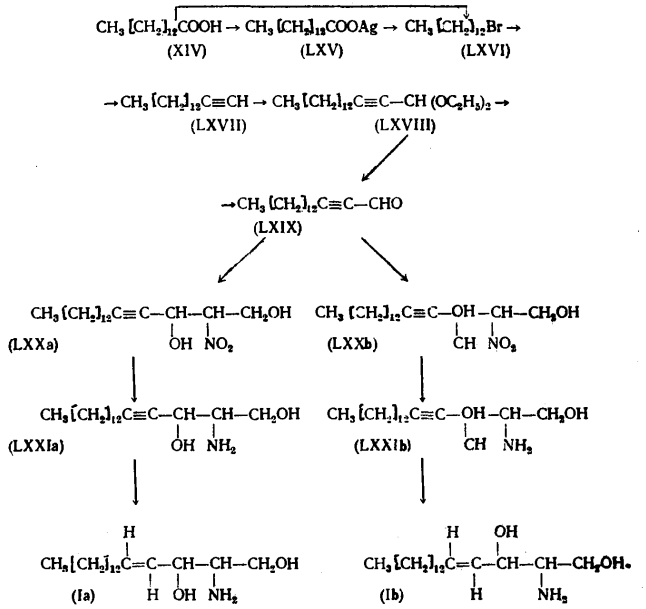
Condensation of the acid chloride (LIX) with ethyl acetoacetate gives ethyl 2-acetyl-3-keto-octadec-4-enoate (LX), which undergoes the Japp–Klingemann reaction with phenyldiazonium chloride under rigorously controlled conditions to give the phenylhydrazone (LXI). Reduction of the latter to the acetamidoester (LXII) with zinc and acetic acid, followed by selective reduction with sodium tetrahydroborate leads to a mixture of diastereomeric alcohols (LXIIIa, b), from which only the *erythro*-isomer (LXIIIa) can be crystallised. When (LXIIIa) is deacetylated with dilute hydrochloric acid in dioxan, the hydrochloride of *erythro*-ethyl 2-amino-3-hydroxyoctadec-4-enoate (LXIV) is formed in relatively low yield, which is due to partial conversion of (LXIV) to the *threo*-isomer. Reduction of (LXIV) with lithium tetrahydroaluminate leads to racemic *erythro*--sphingosine (Ia). The total yield of the latter is about 4%, calculated on the myristaldehyde (XVI).

The relatively accessible myristic acid (XIV) is the starting material in Grob and Gadient's synthesis (Scheme 13) of sphingosine, in which silver myristate (LXV) is converted into tridecyl bromide (LXVI) by the Hunsdiecker–Borodine reaction, or by direct bromination in the presence of red mercury(II) oxide [130] according to the method worked out by the present authors. Condensation of tridecyl bromide with sodium acetylide in liquid ammonia gives pentadec-1--yne (LXVII); this is converted by Iotsich's reaction with orthoformic acid into the diethylacetal of hexadec-2-yn-1--al (LXVIII), which is then hydrolysed to the aldehyde (LXIX). When this is condensed with nitroethanol in the presence of potassium carbonate, a mixture of *erythro*- and *threo*--1,3-dihydroxy-2-nitro-octadec-4-ynes (LXXa, b) is formed; the pure *threo*- (LXXb) and *erythro*- (LXXa) isomers are separated by fractional crystallisation.

Reduction of the nitrodiols (LXX) with zinc and hydrochloric acid leads to a mixture of *erythro*- and *threo*--1,3-dihydroxy-2-amino-octadec-4-ynes (LXXIa, b); *erythro*- and *threo*-sphingosines (Ia, b) are obtained by subsequent reduction of the triple bond with lithium tetrahydroaluminate. The overall yield of *erythro*-sphingosine, calculated on myristic acid (XIV) is about 7%; *threo*--sphingosine (Ib) is obtained at the same time in a yield of about 9%. The *cis*-isomers of sphingosine can be obtained by reducing the aminodiols (LXXI) on $Pd/CaCO_3$.

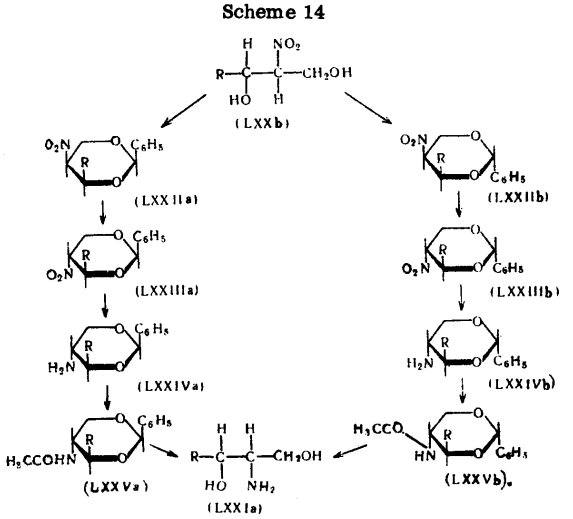
Thus, the more efficient synthesis of Grob opens the way to the preparation of all the possible spatial isomers of sphingosine, which are of great interest in biological studies.

Scheme 13



Because the unnatural *threo*-isomer (Ib) predominates in the latter synthesis, Grob and Gadient proposed a method for the *threo*–*erythro*-isomerisation of sphingosine [129]. For this purpose a mixture of two intermediate cyclic benzal derivatives (LXXIIa, b) is prepared, these being formed in a ratio of 5 : 1 in the reaction of *threo*-1,3-dihydroxy-2--nitro-octadec-4-yne (LXXb) with benzaldehyde in the presence of zinc chloride (Scheme 14; R = $CH_3[CH_2]_{12}C{\equiv}C-$).

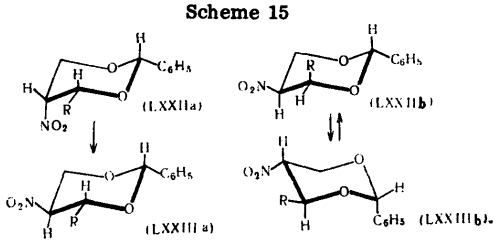
Scheme 14



The cyclic acetals (LXXIIa, b) differ in the orientation of the phenyl group in the 2-position of the 1,3-dioxan ring. Treatment of (LXXIIa) with sodium ethoxide in ethanol results in virtually complete conversion into the epimer (LXXIIIa), and when this reaction is carried out with (LXXIIb), an equilibrium mixture is formed containing the epimer (LXXIIIb) and the starting (LXXIIb) in the ratio 3 : 2.

This kind of difference in the equilibrium position is explained by the greater stability of the most favoured completely equatorial conformation (LXXIIIa) in comparison with (LXXIIa) and the approximately identical stabilities of (LXXIIb) and (LXXIIIb) (Scheme 15).

Scheme 15



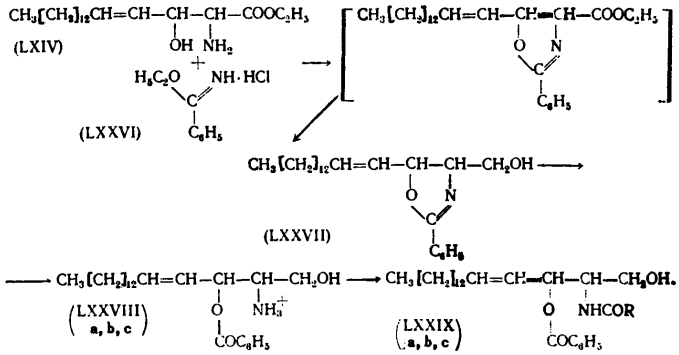
When (LXXIII) is reduced with aluminium amalgam, the amines (LXXIV) are formed, and on acetylation these give *erythro*-5-acetamido-4-(pentadec-1-ynyl)-2-phenyl-*m*-dioxans (LXXVa, b) (see Scheme 14); hydrolysis of the latter gives *erythro*-2-amino-1,3-dihydroxyoctadec-4-yne (LXXIa). The large number of stages and the long time required for some stages are disadvantages of the method. Because of these disadvantages, the present authors have worked out a new method for the *threo–erythro*-isomerisation of sphingosine, the main features of which are described in the following Section.

Grob's method has been successfully used for the synthesis of C_{20}-*erythro*-sphingosine (III) [131] and C_{20}-*erythro*-dihydrosphingosine (IV) [132] and their stereoisomers, which have been isolated in recent years; it has also been used for the synthesis of a number of long-chain amino-diols, homologues of sphingosine [133].

3. Methods of Synthesis of Glycosphingolipids

Natural sphingolipids, in particular glycosphingolipids, contain a free allyl hydroxyl group, and it is desirable that this group should be temporarily blocked during the synthesis [134–137]. With sphingosines (I) as starting materials, this blocking is difficult because of the presence in these bases of a complex system of active centres of similar reactivity in conjunction with an ethylene bond, which makes allyl rearrangements possible. The first important advance was made by Shapiro and coworkers on the basis of their sphingosine synthesis, in which the intermediate *erythro*-ester (LXIV) has a potential primary sphingosine hydroxyl group in a latent form as an ester grouping. Condensation of the *erythro*-ester (LXIV) with ethyl iminobenzoate hydrochloride (LXXVI)‡ and subsequent reduction of the ester group with lithium tetrahydroaluminate gives the oxazoline (LXXVII) (Scheme 16).

Scheme 16



When the oxazoline (LXXVII) is treated with dilute sulphuric acid in tetrahydrofuran, *erythro*-3-*O*-benzoylsphingosine (LXXVIIIa) is formed.

Using *L*- and *D*-tartaric acids, Shapiro [137] separated the sulphate (LXXVIIIa) into antipodes by way of L-*erythro*-3-*O*-benzoylsphingosine *L*-tartrate (LXXVIIIb) and D-*erythro*-3-*O*-benzoylsphingosine *D*-tartrate (LXXVIIIc). Acylation of the sulphate (LXXVIIIa) or the tartrates (LXXVIIIb, c) with a fatty-acid chloride in the presence of sodium acetate–acetic acid buffer leads to DL-, L-, and D-*erythro*-*N*-acyl-3-*O*-benzoylsphingosines (LXXIXa, b, c) respectively; these are then used for the direct synthesis of sphingolipids.

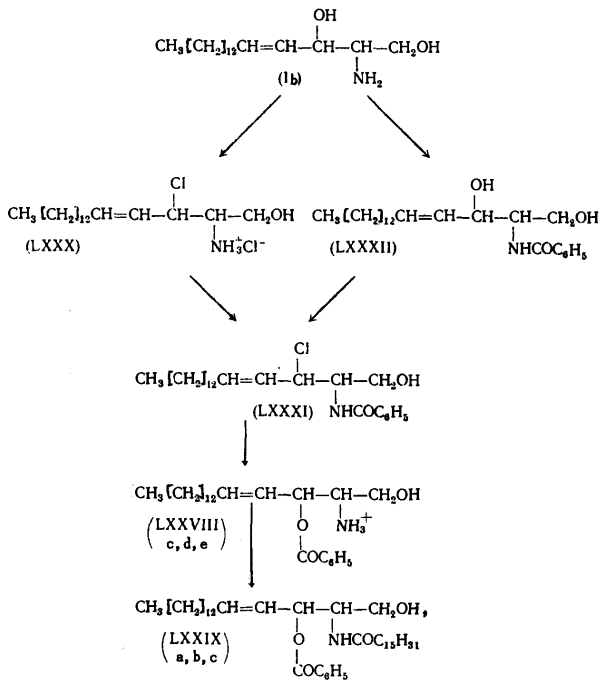
We have developed another method [138] of protecting the allyl hydroxyl group with simultaneous *threo–erythro*-isomerisation; this enables natural derivatives of *erythro*-sphingosine to be prepared from its threo-form (Ib), which is preferentially formed in Grob's synthesis. When a salt of *threo*-sphingosine (Ib) (Scheme 17) reacts with thionyl chloride in chloroform at 20°, *threo-trans*-2-amino-3-chloro-1-hydroxyoctadec-4-ene (LXXX) is formed, and on *N*-benzoylation with benzoic anhydride in the presence of sodium hydrogen carbonate this gives *threo-trans*-2-benzamido-3-chloro-1-hydroxyoctadec-4-ene (LXXXI).

The latter can also be obtained by chlorinating *threo*-*N*-benzoylsphingosine (LXXXII), that is, by changing the order of the stages. It is interesting to note that appreciable quantities of the oxazaline (LXXVII), which is an intermediate in the syntheses of sphingolipids by the Shapiro method (see Scheme 16), is not formed here. Apparently its formation is not favoured energetically [139].

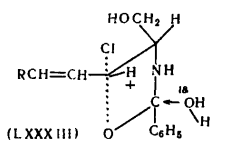
When the β-chloroamide (LXXXI) was heated in aqueous tetrahydrofuran, *erythro*-3-*O*-benzoylsphingosine (LXXVIIId) was obtained; this compound can be used in directed syntheses of sphingolipids. Measurement by amperometric titration of the amount of chloride ions liberated has shown that the reaction is an equilibrium process. It was shown by a special experiment with water containing heavy oxygen [140] that the reaction probably proceeds through a hypothetical transition state (LXXXIII); the regenerated oxygen function of *erythro*-3-*O*-benzoylsphingosinium (LXXVIIId) chloride is formed from the oxygen of the carbonyl group,

‡ Better termed α-ethoxybenzylideniminium chloride (Ed. of (Translation).

Scheme 17



but the carbonyl function of the ester grouping in (LXXIIId) is built up with the participation of oxygen from the water.

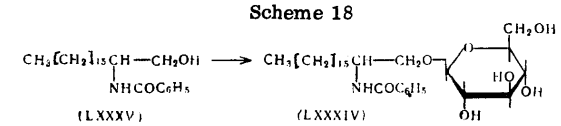


In this example [141,142], separation into antipodes is effected by allowing the chloride (LXXVIIId) to react with the monosilver salt of *D*-tartaric acid [143], followed by fractional crystallisation of the *D*-tartrates of D- and L-*erythro*-3-*O*-benzoylsphingosines (LXXVIIIc, e) formed. Palmitoylation of the chloride (LXXVIIId) or the tartrates (LXXVIIIc, e) leads to DL-, D-, and L-*erythro*-3-*O*-benzoyl-*N*-palmitoylsphingosines (LXXIXa, b, c), identical with the corresponding compounds obtained by Shapiro's method.

4. Synthesis of Cerebrosides and Psychosine

The history of synthetic studies in the glycosphingolipid field begins in 1957, when Prostenik and Krvavica [144] described the synthesis of 1-β-D-glucopyranosyl-*DL*- and 1-β-D-glucopyranosyl-*L*-benzoylsphingine (LXXXIV), in which *N*-benzoyl-*DL*-sphingine or *N*-benzoyl-*L*-sphingine (LXXXV) reacts with α-benzobromoglucose in the presence of mercury cyanide in nitromethane, the reaction product being subsequently saponified with sodium methoxide [145] (Scheme 18).

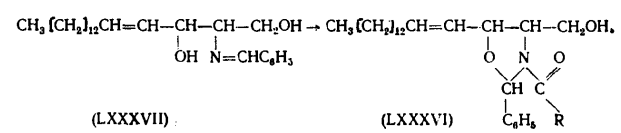
Scheme 18



Kiss was the first to synthesise the dihydrocerebroside [146,147]; he treated dihydro-*N*-tetracosanoylsphingosine with α-acetobromogalactose, and the mixture of α- and β-galactosides, formed as penta-acetates, was subsequently anomerised with titanium tetrachloride. On the basis of this synthesis it was concluded that dihydrocerasine, obtained by hydrogenation of natural cerasine or neurone, has the α-configuration, since it was found to be identical with the synthetic α-galactoside of dihydroceramide (m.p. 186°, $[\alpha]_D$ = +5.31°). In subsequent studies, Shapiro and Flowers [135] showed that this result was incorrect.

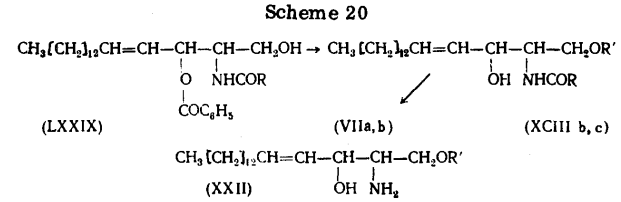
Attempts by Weiss [136] to prepare glycosides of the substituted oxazolidine (LXXXVI), which is obtained by alkylation of *N*-benzylidenesphingosine (LXXXVII) (see Scheme 19), were unsuccessful, as were the attempts of Shapiro to prepare a glycoside of the oxazolidine (LXXVII) (see Scheme 16); these failures were because of the extremely low reactivity of the hydroxyl group in these compounds, and also because of the sensitivity to alkali of the small amounts of glycoside formed.

Scheme 19



Shapiro and Flowers [135] were the first to synthesise cerebrosides (VII) from protected ceramides (LXXIX) obtained by the method described in the previous Section. Condensation of benzoylceramides (LXXIX) with α-acetobromogalactose or α-acetobromoglucose in the presence of mercury cyanide and subsequent saponification of the protecting groups leads to β-D-galacto- and β-D-gluco-cerebrosides (VII) (Scheme 20), identical in physical properties (infrared spectrum and $[\alpha]_D$) with natural cerasine and phrenosine, and with the cerebroside that is stored in the human spleen in Gaucher's disease.

Scheme 20

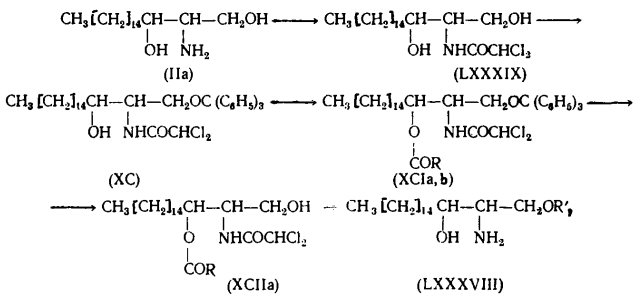


VIIa, R′ = $CH_3[CH_2]_{22}$, R′ = glucose; VIIb, R = Cl_2CH, R′ = galactose;
XXII, R′ = galactose; XCIIIb, R = $CH_3[CH_2]_{22}$, R′ = lactose;
XCIIIc, R = $CH_3[CH_2]_{14}$, R′ = lactose.

Shapiro and coworkers [137] have also described the preparation of psychosine (XXII) — a precursor of cerebrosides in biosynthesis [148] — and its dihydro-derivative (LXXXVIII), which is of interest in biosynthetic studies, particularly the synthesis of cerebrosides labelled in the fatty acid residue. The dichloroacetyl group was found to be the best group for the temporary protection of the amine function in psychosine (XXII) and dihydropsychosine (LXXXVIII). Psychosine (XXII) is obtained in the same way as the cerebrosides (VII) (see Scheme 20), the dichloroacetamide (VIIb) formed being hydrolysed by boiling with barium hydroxide.

A new method was worked out for the synthesis of dihydropsychosine (LXXXVIII) (see Scheme 21).

Scheme 21



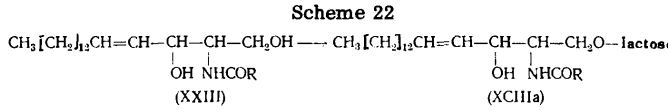
where (a) R = $-C_6H_5NO_2$-*p*; (b) R = C_6H_5; (c) R′ = glucose.

When dihydrosphingosine (IIa) reacts with methyldichloroacetate, the amide (LXXXIX) is formed; the primary hydroxyl group of this compound is temporarily tritylated and the secondary hydroxyl group is then *p*-nitrobenzoylated, (LXXXIX) → (XC) → (XCIa), since the benzoyl derivative (XCIb) is difficult to purify. Removal of the trityl protecting group with dilute acetic acid leads to the dichloroacetamido-ester (XCIIa), which is converted into dihydropsychosine (LXXXVIII) in the usual way. Later it was pointed out [149] that natural derivatives of *erythro*-sphingosine could be synthesised by this new method (see Scheme 21). This is particularly interesting since it provides a shorter synthetic route from natural *erythro*-sphingosine to the sphingolipids.

5. Synthesis of Cytolipin H

Schram and coworkers [150] synthesised the lactoside (XCIIIa), which is similar in structure to cytolipin H, using as a starting material ceramide (XXIII) obtained by enzymatic hydrolysis [151] of sphingomyelin from ox heart (Scheme 22). The infrared spectra of the lactoside (XCIIIa) and cytolipin H are almost identical, but their specific rotations differ ($[\alpha]_D$ = +2.1° and -10.8° respectively).

Scheme 22



In 1964 a synthesis of 1-*O*-β-D- and 1-*O*-β-DL-lactosyl-*N*-lignocerylsphingosines (XCIIIb) was described [152], but experimental details were not published; the method used was that developed by Shapiro for the preparation of cerebrosides (see Scheme 20). The lactoside (XCIIIb) was found to be identical in physicochemical and serological properties with cytolipin H. The work of Schram [150] has been subjected to critical examination. In particular, the probable ambiguity in lactoside formation by the unprotected ceramide (XXIII) has been pointed out; this has been related to the increased angle of rotation of the lactoside (XCIIIa).

The lactosides of *erythro*-*N*-palmitoylsphingosine (XCIIIc) and its *threo*-isomer, which are similar in structure to cytolipin H, have been prepared independently by the present authors [141,142], using the new method of synthesising sphingolipids described above [138] (see Scheme 20).

IV. BIOLOGICAL PROPERTIES

1. Immunological Properties

Recent studies in connection with the cancer problem have shown that there are significant differences in structure and biochemical composition between normal cells and tumour cells; these differences result from malignant degeneration of the tissues [153].

It has now been shown that all glycosphingolipids have the properties of organ-specific and tissue-specific haptens [154]. It is possible that glycosphingolipids, occurring as they do in membranes, participate in immunological control of cell growth [155].

Rapport and Graf made an extensive study of glycosphingolipid haptens. Using the method of complement fixation, they were the first to show that the individual lipid hapten isolated from human epidermoid carcinoma, cytolipin H, is a tissue-specific substance in a number of malignant neoplasms, such as carcinoma of the lungs, spinal cord, kidneys, and throat; Hodgkin's granuloma; bone sarcoma; lymphosarcoma; myelogenic leukaemia; and malignant melanoma. On the other hand, cytolipin H does not react with antiserum against carcinoma of the rectum or colon or epidermoid carcinoma [53,156]. Large quantities of this compound occur in the spleen of cancer patients, and small quantities occur in their livers, but none has been detected in the kidney tissues.

Repeated attempts to prepare antibodies that react with lipid extracts of cancer tissue by injecting tissue fractions of normal organs have been unsuccessful. This indicates that cytolipin H is present in only insignificant amounts, if at all, in normal organs [157]. However, Japanese biochemists [37,50,59,60] have isolated a number of glycosphingolipids, especially lactosylceramides, from various organs, including kidneys from healthy human subjects.

Immunological examination of dihydrocytolipin H, [57] and also of synthetic D- and DL-*erythro*-lactosyl-*N*-lignocerylsphingosines [158], has shown that the presence of a double bond and optical activity in the lipid part of the molecule are not essential for the immunological activity of cytolipin H. However, a change in the structure of the carbohydrate part of the molecule leads to loss of activity [159]. Rapport therefore concluded that the immunological specificity of glycosphingolipid haptens, and particularly of cytolipin H, depends, largely if not entirely, on the structure of the carbohydrate part of the molecule [61], and he has recently confirmed this conclusion [66]. The lipid residues only play a part in the localisation of the hapten in the cell membrane.

Schram and coworkers [150] accepted this point of view too readily; they thought that lactosides of any aliphatic or aromatic alcohols must behave in the same way as cytolipin H in the complement fixation reaction.

Attempts to immunise rabbits with cytolipin H, even in the presence of pure auxiliary lipids — lecithin and cholesterol — proved unsuccessful. Specific antibodies were obtained when immunisation was carried out with a mixture of cytolipin H and total tissue lipids.

The simplest glycosphingolipid, galactocerebroside [159,160], is an organ-specific lipid of brain [161]. The antiserum obtained by immunisation of rabbits with fractions of human and cow brain is active in the complement-binding reaction with galactocerebroside [160] in the presence of auxiliary

lipids, but it does not react with glucocerebroside or with cytolipin H.

The globoside isolated from human kidney and named cytolipin K is an organ-specific kidney hapten [66]. Forssman's hapten from sheep erythrocytes also contains sugar, fatty acid, and sphingosine residues characteristic of glycosphingolipids [61].

Yokoyama and coworkers [162] have proposed a useful method for the preparation of antiganglioside sera. When immunisation was effected with gangliosides deposited on the surface of erythrocytes, a high antibody titre was obtained. The specificity of the antiganglioside antibodies was demonstrated by the haemagglutination reaction, which is scarcely observed with erythrocytes covered with asialogangliosides.

In common with some other compounds, brain gangliosides inhibit the haemagglutination reaction with antibodies against Rhesus-positive erythrocytes [163], which indicates that gangliosides and blood-group antigen are immunologically similar [164]. However, antiganglioside serum does not react with Rhesus-positive erythrocytes in the haemagglutination test. This appears to be a reflection of fine structural differences between the ganglioside and the antigen determinant (possibly a complex lipopolysaccharide [165]) of Rhesus-positive human erythrocytes.

Two ganglioside-like compounds have also been separated from human erythrocytes [105], which, in addition to mucopolysaccharides [166], are substances characteristic of blood group A. These substances differ in physicochemical properties and in composition from the human erythrocyte globosides to which the group activity of the human blood groups A, B, O, and AB is ascribed [167]. Here the activity appears to be due to the presence of active mucopolysaccharides as impurities in the preparations.

In accordance with the classical method of diazo-fixation of Landsteiner [169], the reaction of diazotised *N*-*p*-aminobenzoyldihydropsychosine with proteins [168] gives artificial antigens. Immunochemical analysis by the precipitation method showed that the antiserum obtained by immunisation with such artificial albuminolipid antigens contains at least two types of antibody, antidihydropsychosine and antialbumin antibodies. However, the question to what extent antibodies obtained in this way will be complementary to natural glycosphingolipid haptens remains open.

2. Biological Activity of Sphingosine and Cerebrosides

The high-molecular-weight lipoprotein enzyme thromboplastin catalyses one of the stages in the complex process of blood coagulation [170]. The anticoagulant activity of sphingosine [171,172] is associated with its antithromboplastic [173] (that is, antienzyme) activity. This was first demonstrated in chicken plasma [174].

The use of comparatively small quantities of sphingosine in the presence of a lipid blood-coagulation activator has no inhibiting effect, but, if sphingosine is first incubated with chick blood plasma and the lipid activator is then added, the rate of coagulation is greatly increased compared with that using the lipid activator alone.

Thus, the way in which sphingosine acts depends on its concentration, on the concentration of lipid activator, and on the individual properties of the plasma. Synthetic *erythro*- and *threo*-dihydrosphingosines were found to be weaker coagulation inhibitors than sphingosine; *N*-benzoyldihydrosphingosine and triacetylsphingosine are entirely inactive. Synthetic homologues of sphingosine show the greatest activity when the chain contains 17–18 carbon atoms [133]. The presence of a double bond, free hydroxy- and amino-groups, and a long hydrocarbon chain are therefore necessary for anticoagulant activity [174].

When cerebrosides are introduced into the human organism or into experimental animals, more cholesterol is excreted with the faeces and the level of cholesterol in the blood is reduced [175]. The mechanism of this process is still unknown.

3. Neurophysiological Role of Gangliosides

Recently a number of workers have noted the important part played by the sialic acid components of gangliosides.

Van Heyningen showed in vitro experiments [176] that the gangliosides of ox brain are receptors for tetanus toxin [177], and also for such drugs as strychnine, brucine, and thebaine, which have similar neurophysiological activity [178]. The fixing power of the gangliosides is proportional to the number of sialic acid residues present in the molecule, but it also depends on the structure of the whole carbohydrate part of the molecule [179]. For example, hematosides isolated from horse brain or horse erythrocytes, which do not contain hexosamine, and the ganglioside that accumulates in the spleens of patients with "Tay-Sachs'" disease are virtually inactive [178].

The fixation of tetanus toxin by gangliosides is strictly specific for this toxin, and the non-specific inactivation of diphtheria and staphylococcal toxins by these compounds, which has been noted by North and Doery [180,181] has nothing in common with the fixation of tetanus toxin; this toxin is not inactivated at all [176]. Gangliosides also interact with serotonin, tryptophan, and related compounds, but not with γ-aminobutyric acid, β-hydroxybutyric acid, histamine, adrenaline, or noradrenaline [178].

The process by which the tetanus toxin is fixed by the ganglioside receptor in nerve tissue is directly related to the mechanism of action of the toxin. This is confirmed by the high specificity, and also by the fact that the gangliosides and the synapses inhibited by the toxin are found in the grey matter of the human brain.

The reaction of gangliosides with bacterial endotoxin that produces fever leading to disorders of the heat-regulating function of the body has also been described [182].

It may be that the reaction of the ganglioside with the toxin or with the drugs mentioned above is the first step that leads to the biochemical attack on which the pharmacological action of these compounds is based. On the other hand, the receptor may be responsible for adsorption of the toxin at the infection sites, and for its localisation in the nerve cells with subsequent centripetal transfer along the nerve columns to the site of activity in the brain or spinal cord. However, none of these hypotheses can be accepted without reservation.

Brain gangliosides are mainly associated with fractions of subcellular particles [183], which have an affinity with basic proteins [184], especially with microsoma [185] and, to a lesser degree, with mitochondria. They are readily extracted from brain tissues, but when added to a suspension of subcellular fractions of basic proteins, for example,

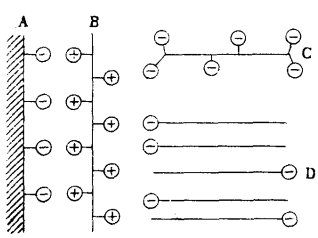
protamine, the gangliosides cannot be separated [142]. Evidently the natural gangliosides, which are acid components of lipid-rich membranes that participate in active cation transport, are linked to the basic proteins by ionic forces. This accounts for the opposite effects of these proteins and gangliosides on the excitability of the brain.

The normal brain exhibits continuous electrical and metabolic activity, which can be stimulated, particularly by electrical impulses [187]. Isolated brain tissue in a suitable nutrient solution can breathe and respond to electrical stimuli by showing increased assimilation of glucose and oxygen [188]. When such a system is cooled to 0°, the respiratory response to electrical stimulation is only 15% of the maximal reaction of normal tissue, but this response increases to 52–80% when 60–120 μg per mg of gangliosides is added. Evidently, when the tissue is cooled, the histones — which are basic proteins linked with ribonucleic acid in cell nuclei — lose their capacity of forming nucleohistone gel [184]. They separate from the RNA and migrate out of the nuclei, blocking the acid sections of the membranes. This stops reversible transfer of potassium ions in cerebral tissue after stimulation. Added gangliosides associate with these basic proteins and neutralise their activity [189-192].

Inhibition of brain excitability by protamines occurs in the same way as when cooling is applied, and it is abolished by gangliosides in exactly the same way.

Ordinary acid reagents cannot replace gangliosides. Neither *N*-acetylneuraminic acid nor L-glutamic acid restores excitability. Monoacid compounds, which cannot form aggregates, can only neutralise the basic groups of protamine, but this is not sufficient to restore excitability, which is associated with the presence of acid groups on the external surface of the membrane (see Scheme 23). On the other hand, polyacid compounds such as sialomucopolysaccharides, chondroitin sulphate, poly-L-glutamic acid, the aromatic hexasulphonic acid suramin, or micellar aggregates of such compounds as lecithin, phosphatidylethanolamine, sphingomyelin, and phosphatidylserine — compounds of widely different structure — all behave like gangliosides [193].

Scheme 23



Hypothetical interaction between acid areas of tissue (A), basic proteins (B), and polyacid molecules (C), or micellar aggregates (D).

This activity of gangliosides is higher than the activity of all other compounds and it increases with the number of sialic acid residues in the ganglioside. It is noteworthy that gangliosides restore the excitability of brain tissue and they are present in concentrations close to the critical concentration for the formation of micelles. Individual molecules of gangliosides probably first react with tissues that bind protamines, and then they combine to form micelles.

A similar explanation has been advanced for the metachromatic properties of gangliosides [194], that is, the capacity to form associations with suitable basic dyes (for example, Toluidine Blue or Pyocyanine [195]) that differ in colour from the dye itself [196]. This effect is due to association of the dye molecules with suitably arranged acid groups of the compounds being dyed [197]. A molecule of thiazine dye appears to combine with the acid groups of micellar gangliosides as a result of ionic forces, and it then undergoes association, due to secondary forces, with the formation of metachromatic dimers and polymers. The effect disappears in organic solvents, apparently because of a change in the structure of the ganglioside micelle, sialic acid residues being removed from the surface of the sphere, and also because of interaction of the dye and the solvent, which destroys the metachromatic aggregate. Because it can react with gangliosides, protamine also inhibits the metachromatic reaction with Toluidine Blue.

Using a histochemical method based on metachromatic reactions, Koenig [198] studied the localisation of the gangliosides in the nerve system, and he showed that the glycolipoprotein cytoplasmprotein granules (the so-called synaptic vesicles) containing acetylcholine [199] are also rich in gangliosides. In this connection, Burton and coworkers [109,200] put forward the hypothesis that gangliosides play a part in the transmission of nerve impulses through synapses in accordance with the concepts of a neuro-humoral mechanism [109,200]. At present, however, these concepts have given way to the idea [201] that acetylcholine functions in a uniform manner in synaptic connections and conducting axon membranes.

From the foregoing it is clear that gangliosides play an essential part in neurophysiological processes, but our knowledge in this field is still very unsatisfactory.

Further extension of our ideas on the significance of glycosphingolipids in biological systems will probably be mainly determined by the development of biochemical, biophysical, and synthetic work in this field. The problems that now have to be solved are concerned not only with the elucidation of the primary structure of new, hitherto unknown, types of glycosphingolipids, but also with establishing the actual shapes of these compounds in three-dimensional space, that is, of the forms in which they carry out their biological functions.

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While this manuscript was being prepared for the press, interesting reviews appeared on the chemistry of gangliosides [202], and sulphatides [203], and on methods of analysis of glycolipids [204], in addition to a review article on the immunochemical properties of glycolipids [205]. Further studies have led to the isolation of a number of new sphingosine bases from animal tissues [206-208]. Thus, twenty compounds of this type are known already; these differ in chain length, number of hydroxyl groups, and degree of unsaturation. A number of new glycosphingolipids have been isolated, including *O*-acylcerebrosides from ox brain [209], and also gangliosides from human brain [210,211], leucocytes [212], and placenta [213].

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THE STUDY OF ELEMENTARY CHEMICAL REACTIONS BY THE MOLECULAR BEAM METHOD

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I. INTRODUCTION

In 1955 a paper[1] was published, demonstrating convincingly for the first time the real possibility of studying chemical reactions accompanying the collision of the molecules of two intersecting beams. It is no exaggeration to say that the publication of this paper opened up a new stage in studies of the mechanism of bimolecular gas reactions and originated a new line of research.

This review examines the present position and some immediate prospects in the use of intersecting molecular beams to study the mechanism of bimolecular gas reactions.

Section I gives a general picture of the molecular beam method, presents some theoretical concepts used in the examination of kinetic problems within the framework of collision theory, and finally discusses the analogy between collisions leading to chemical changes and those responsible for ordinary transfer phenomena in gases.

Section II, after a brief discussion of the experimental technique, describes the chief methods used in the analysis and interpretation of the experimental data.

The concluding Section III is devoted to a detailed examination of the chief experimental results obtained by molecular beam studies of some bimolecular chemical reactions.

Most chemical processes are complex multistage reactions, and only a relatively small proportion correspond to single-stage elementary reactions. It is obvious, however, that each stage in a complex process can in a certain sense be regarded as an elementary reaction, and study of the elementary reactions can in principle lead to a better understanding of the characteristic features of the process as a whole. This explains why in chemical kinetics there is great interest in the study of elementary chemical reactions, of which bimolecular reactions form the most commonly encountered class. The subsequent discussion deals chiefly with these reactions.

One of the main tasks in chemical kinetics is to determine the principal conditions (energetic, configurational, etc.) which must be satisfied by molecules if a chemical reaction is to take place between them. This must be regarded as the fundamental problem, since the frequency with which these conditions are realised in molecular collisions influences the rate of the process and at the same time is comparatively readily determined by familiar methods within the framework of equilibrium statistics, whose applicability is generally assumed.

On the other hand, if the equilibrium approximation is inapplicable, the problem of finding the perturbed distribution functions will also include in the initial stage the determination of the chief microscopic conditions for reaction to take place on collision of the molecules.

The classical methods of kinetic studies[2] cannot take us beyond the limits of the phenomenological Arrhenius equation, leaving to the research worker a considerable degree of freedom in the interpretation of the intimate details of the mechanism of the reaction being studied. Since the activation energy and the steric factor are found by effective statistical averaging over a large number of energy

states and the corresponding collision parameters, these characteristics are insufficient for a complete understanding of the elementary act in a chemical change. Thus there is no guarantee even that theories which provide an obviously correct description of reaction rates are based on correct original hypotheses regarding the mechanism of the elementary process.

This situation makes it extremely desirable to develop and use kinetic methods which are free from this uncertainty. The molecular beam method[3] satisfies these requirements, since, in addition to specifying the translational energy of the colliding particles, it also permits the selection of definite internal stages. In the ideal case it enables a chemical reaction to be conducted with complete control of the energy states and even of the orientations of the reacting molecules.

The molecular beam method is based on the use of a beam of atoms or molecules, produced by a suitable method, as a subject for study, either immediately after its production (in this case the particles of the beam "carry" information on the thermodynamic and physicochemical state of the gas in the formation region) or after the beam has been acted on in some way. The nature of the action on the particles of the beam and the methods used may vary: in all cases — irradiation with a beam of light, reflection from a solid surface, the action of electric or magnetic fields, collision with particles of another beam, etc. — we obtain information on the effects produced by the action. The importance of the molecular beam method in chemical studies is that it is possible in an experiment to record the direct effect of a fairly exactly localised interaction between particles capable of undergoing reaction, so that the effect is not obscured by side reactions or, as is often the case in chemical processes, competing reactions. It is thus possible to isolate an elementary process and to study it over a wide range of controlled collision energies; the localisation of the collision region effectively frees the reaction from the influence of the walls of the reaction vessel. A fairly detailed discussion of the possible applications of the molecular beam method can be found in recent reviews[3-5], and this makes it possible to restrict the present review to a discussion of studies of bimolecular gas reactions.

The ideal arrangement for an experiment to study chemical interaction between molecules corresponds to the use of two intersecting collimated beams homogeneous with respect to velocity, or of one such beam passing through a layer of relatively immobile molecules in a bombarded target. In these cases the emission of the reaction products can be observed within a very narrow range of angles about a certain direction determined by the kinematic conditions to be examined below.

The quantity of reaction products makes it possible to determine the reaction probability or cross-section, and variation of the velocities and internal energies of the particles permits the dependence of the cross-section on these parameters to be found. The position of the maximum and the width of the angular distribution of the products enable in some cases conclusions to be drawn regarding the nature of the distribution between the products of the energy liberated in the reaction, or conclusions regarding the lifetime of the intermediate complex. It is also possible to determine directly the internal energy of the reaction products and the spectrum of their velocities. Thus the extent to which the equilibrium distribution is broken down by the chemical reaction can be established. The reaction products can in turn be used as a beam for secondary scattering.

These are the basic possibilities of the molecular beam method. The level of experimental technique employed does not always permit us to realise them completely. As will be subsequently seen, however, even partial utilisation of these possibilities has enabled us to observe reaction-mechanism details which are quite inaccessible by ordinary methods. The continuous development of experimental technique in the last ten years is bringing these experiments closer to the ideal.

What is the relationship between the microcharacteristics of a chemical reaction (cross-section, threshold energy), determined in experiments with intersecting beams (the same characteristics are obtained in the theoretical analysis of elementary processes), and parameters such as, for example, the rate constant and the activation energy? This question is part of the more general question of the relationship between the microscopic and the macroscopic properties of gaseous systems. It is useful to follow this relationship and to recognise the main assumptions necessary for unambiguous conversion from one set of parameters to the other. Following Eliason and Hirschfelder[6], let us consider a reaction of the type A + B → C + D, taking place in a gas exhibiting a certain distribution of translational and internal energies. By analogy with the analysis of transport in a gas (there is an extremely sound basis for this analogy), it is convenient to regard particles with different internal states (characterised symbolically by the quantum numbers i, j, k, and l) as separate components. This approach is further justified by the fact that intuition suggests that the reactivity should depend on the internal state of the collision partners.

The partial rate of a reaction of the type $A_i + B_j \rightarrow C_k + D_l$ is given by the usual relationship

$$\left(-\frac{dn_{A_i}}{dt}\right)_{jkl} = k_{ij}^{kl}(T)\, n_{A_i} n_{B_j}, \qquad (1)$$

where n_{A_i} and n_{B_j} are the densities of the molecules A_i and B_j, and $k_{ij}^{kl}(T)$ is the partial rate constant. The overall rate of the chemical reaction (A + B → C + D) measured in kinetic experiments will then be the sum of the partial rates:

$$\left(-\frac{dn_A}{dt}\right) = \sum_{ij}\sum_{kl} k_{ij}^{kl}(T)\, n_{A_i} n_{B_j}. \qquad (2)$$

From kinetic theory, equating the partial reaction rate to the number of collisions leading to reaction[2], we can readily obtain the following relationship in the classical approximation

$$k_{ij}^{kl} = \iiiint f_{A_i} f_{B_j} \overline{I}_{ij}^{kl}(E, \theta\varphi)\, g_{ij} \sin\theta\, d\theta\, d\varphi\, dv_{A_i}\, dv_{B_j}, \qquad (3)$$

where f_{A_i} and f_{B_j} are the normalised distribution functions for the velocities $\mathbf{v}_{A_i}$ and $\mathbf{v}_{B_j}$, and $\overline{I}_{ij}^{kl}(E, \theta, \varphi)$ is the differential cross-section for the collision of molecules in states i and j with relative energy E, leading to the formation of product molecules in states k and l, moving at angles θ and φ to the direction of the relative initial velocity g_{ij}. Since in expression (3) only $\overline{I}_{ij}^{kl}(E, \theta, \varphi)$ depends on the angles θ and φ, we can, by integrating with respect to the angles, obtain a new quantity $C_{ij}^{kl}(E)$ — the so-called total reaction cross-section

$$C_{ij}^{kl} = \iint \overline{I}_{ij}^{kl}(E, \theta, \varphi) \sin\theta\, d\theta\, d\varphi. \qquad (4)$$

In principle, these two quantities (C_{ij}^{kl} and $\overline{I}_{ij}^{kl}$) represent the final results of both theoretical (quantum-mechanical or classical) calculations and experiments with intersecting beams.

The relationship between these microscopic characteristics and the reaction rate (2) is conveniently followed from the diagram[6] (Fig. 1). If the quantity $P_{ij}^{kl}(E, b, \eta, \theta, \varphi, K)$ is the probability that the collision of molecules of types A_i and B_j (involving the formation of a quasi-molecule with a set of quantum numbers K), with initial impact parameter b, azimuthal angle η, and relative energy E, will lead to the production of molecules C_k and D_l, moving at angles of θ and φ in the [coordinate] system of the centre of mass, the diagram shows the possible routes from the quantity $P_{ij}^{kl}(E, b, \eta, \theta, \varphi, K)$ to the rate constant for the reaction $A + B \rightarrow C + D$. It can be seen from Fig. 1 that in the first stage the corresponding averaging can be carried out in three ways — with respect to the values of K, the initial parameters b and η, and the final parameters θ and φ — each arrow in the diagram representing the successive procedure of averaging with respect to the quantities which are not present in the argument to which the arrow points (the use of arrows is of fundamental significance, since movement in the opposite direction is generally associated with ambiguity). This ambiguity is the main obstacle to verification of the correctness of the original theoretical models by means of ordinary kinetic data. The limited nature of the information on reaction mechanism contained in the averaged quantity $k(T)$ is thus fairly obvious.

The value of the molecular beam method when applied to chemical problems is related to the possibility of studying the mechanisms of the elementary processes corresponding to the lower branches of the diagram in Fig. 1. The unique achievements of the method are that the results obtained on the one hand stimulate the theoretical solution of the problem of the elementary act in a chemical transformation and on the other create the necessary basis for solution of the statistical problem of determining the perturbations of the equilibrium distribution function resulting from the chemical process. The particular solution of the statistical problem for the non-equilibrium situation is associated with the names of Chapman and Enskog, who examined the phenomenon of molecular transport in gases.

There is a very close analogy between the description of the rate of a chemical reaction in a gas and the description of transport phenomena (i.e. viscosity, thermal conductivity, diffusion, etc.)[7]. Before the publication of the well-known studies by Chapman and Enskog[8], the study of transport phenomena was of a particularly phenomenological character, whose defects have become especially clear in recent years. Within the framework of this approach it was almost impossible to predict the behaviour of a substance under conditions differing from those under which the experiment was carried out. The requirements of the technique, which penetrated into a range of temperatures which could not be reproduced in laboratory equipment, emphasised still further the limited nature of this approach (the situation was aggravated by the possibility of dissociation of the gas at high temperatures).

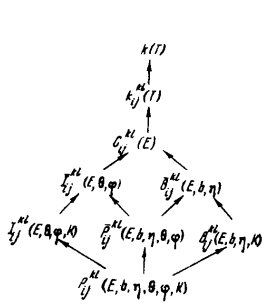

Fig. 1. Diagram illustrating the relationship between the microscopic and the macroscopic characteristics of a chemical transformation.

Chapman and Enskog reduced the description of transport phenomena in monatomic gases to a single basis — the intermolecular forces — and, for a known law of variation in these forces with distance, the determination of the kinetic coefficients became a comparatively simple computational problem. In this way the emphasis in the study of the kinetic properties of gases is being transferred to the problem of determining intermolecular forces[9]. It is extremely tempting to arrive at a similar situation in chemical problems; the immense number of possible collision partners and the limited range of attainable temperatures in this case also lead quite naturally to the necessity for finding a single basis for the description of the phenomena of chemical interaction. In this sense the transition-state theory plays a part which is in some ways analogous to the microscopic approach to the description of transport phenomena. Within the range of applicability of the corresponding approximations, the kinetics of a chemical reaction to a considerable extent reduces to a simple (from the physical viewpoint) basis — the intermolecular forces between the approaching particles. Although in the case of chemical kinetics it cannot yet be said that the main emphasis of research should be transferred entirely to the study of intermolecular forces, there is no doubt that, for reactions with a high energy threshold, studies at this level will be fruitful. Until recently, the only and insufficiently reliable source of information on intermolecular forces for chemically interacting partners was the so-called semi-empirical method of Eyring. The use of the molecular beam method combined with fast computers is opening up another source of such information. This possibility is of great promise and is discussed in Section III.

II. TECHNICAL REALISATION AND INTERPRETATION OF EXPERIMENTS WITH MOLECULAR BEAMS

Since a recent paper[3] described in detail the present state of the experimental technique of the molecular beam method, we shall restrict ourselves to an examination of certain fundamental elements of the technique of working with intersecting beams and the most recent achievements in this field.

As noted above, the chief advantage of the molecular beam method is that it permits control of the energies of the interacting molecules. The only method for isolating particles with a fixed velocity from the beam is by using mechanical selectors[3]. When both beams consist of particles with a fixed velocity, however, there is a sharp decrease in the intensity of the recording signal of the reaction products, and the situation is aggravated by the need to synchronise the arrival of the particles in the region where the beams intersect. At present, therefore, the use of selectors is restricted to one of the beams[10], and quantitative allowance can be made for the scatter thus preserved in the relative collision energies, by analysing the velocities of the products by means of a second velocity

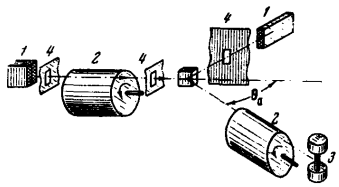

Fig. 2. Diagram of a typical experimental assembly for studying chemical reactions in intersecting beams with thermal velocities:
1) beam sources; 2) mechanical selectors for isolating particles with a given velocity; 3) movable receiver for recording both elastically scattered molecules and reaction products; 4) collimating slits.

selector. This modification must at present be regarded as representing the best arrangement for an experiment with intersecting beams (Fig. 2).

A simple method for ensuring that the collisions being studied involve beams of particles with fixed velocities is to use beams of relatively high energy (10–1000 eV), passing through a gas target, whose molecules can be regarded as virtually stationary. High-energy beams are usually produced[3] by neutralising ion beams which have been brought to fixed velocities electrostatically. An assembly has been described[11] for obtaining fast beams of almost any active atoms, radicals, or molecules in the energy range 600–4000 eV. A typical example of the use of high-energy ion beams can be found in a study[12] of the reaction $N_2^+ + D_2 \rightarrow N_2D^+ + D$.

The number of reactions which can be studied at present is limited by the necessity of ensuring that the particles of the intersecting beams have a relative collision energy greater than the energy thresholds of the reaction. Another restriction is imposed by the method of recording. The most widely used product detector is the differential surface-ionisation detector[1]. The use of this phenomenon for recording obviously limits the possible reaction products to compounds containing alkali-metal atoms. Thus the reactions which have been most extensively studied are those in which one of the partners is potassium, caesium, or rubidium (or, less satisfactorily, lithium or sodium).

This restriction can be overcome by using universal ionisation detectors[3], in which the molecules being studied are ionised by electron impact. Positive ions can be collected by a collector and measured by standard methods. A recently proposed modification[13] uses neutralisation of the space charge in a diode by the positive ions. When ionisation by electron impact is used, the possibility of dissociation must be borne in mind. Partial allowance for this effect can be made by mass-spectrometric observation of the products.

The universality of ionisation detectors is also a weakness, since the total recording signal is influenced not only by the reaction products but also by the residual gases and particles which have undergone elastic scattering. The influence of the residual-gas background in a laboratory apparatus cannot always be eliminated by improving the vacuum conditions; an effective method of reducing this effect is to modulate the beam and record only the modulated component of the detector current[3]. There still remains, however, the difficulty of recording the products in the region of the "shadow" of the original beam, since it is impossible to separate the currents from the elastically scattered molecules and possible reaction products. This difficulty can be overcome by fitting the receiver with an additional mass filter. A device for selecting ions according to mass can be constructed using either a static magnetic field[14] or the high-frequency electrostatic field of a quadrupole lens[15]. Analysers of the time-of-flight and radio-frequency types also have certain advantages, but when these are used it is more difficult to eliminate the influence of the residual-gas background. The most convenient for these purposes are analysers of the quadrupole type[15,16], which have a high transparency (low ion loss), effective resolution over a wide range of mass numbers and small size. Thus an instrument has been described[16] which makes it possible to record simultaneously ion currents differing by 8 orders of magnitude. These possibilities are of particular interest in connection with the prospects provided by the use of so-called gas-dynamic sources of molecular beams[3], with which beams of heavy molecules having high velocities can be obtained; these, however, contain a certain quantity of light "runaway" gas (H_2).

Interesting possibilities related to the problems examined here are provided by making use of the action of electric and magnetic fields on the beams. The simplest involves the use of an inhomogeneous magnetic field to separate a mixed beam of original atoms and product molecules in the region of the "shadow". The original beam usually comprises paramagnetic alkali-metal atoms; the product molecules are generally diamagnetic, so that, when the mixed beam is passed through an inhomogeneous field, the deflection of the atoms makes it possible to achieve spatial separation of these components. As a result, the receiver is able to record them separately. This method has been used by Herm et al.[17]; in some cases analogous results can be obtained by velocity analysis of the mixed beam using a mechanical selector.

It is more tempting[18,19] to use an inhomogeneous electric field to analyse the rotational states of the reaction products. For a substitution reaction with a marked change in the reduced mass, the initial orbital angular momentum will be converted into the internal angular momentum of the product molecule. As a result of the law of conservation of angular momentum, the rotation is polarised, since the internal momentum vector of the product molecules will coincide with the vector of the initial orbital momentum, perpendicular to the vector of the initial relative velocity. The polarisation will have a marked influence on the deflection of the molecules in an inhomogeneous electric field. Thus analysis of the rotational state of the products makes it possible to establish the influence of the initial orbital momentum on the probability of reaction on collision, i.e. to determine which orbital momenta (impact parameters) make the main contribution to the reaction cross-section. This analysis may allow[19] separation of the vibrational and rotational components of the internal energy of the products.

Let us now examine qualitatively the methods for treating the information obtained in experiments with molecular beams. The primary information obtained in an experiment is the angular distribution of the reaction products, the dependence of the yield of products (total or differential) on the relative collision energy of the particles in the beam, and finally the velocity spectrum of the products moving in a given direction. This primary information must be

interpreted on the basis of various models. In addition to direct recording of the reaction products, study of the elastic scattering of the particles of intersecting beams is also of considerable interest for obtaining the characteristics of a chemical reaction. Thus is due to the fact that the "entry" sections of the potential-energy surface of the reaction for elastic and "inelastic" scattering are the same with adiabatic reactions. Qualitative examination of the characteristic features of elastic scattering is necessary for an understanding of the material which will be presented subsequently.

The dependence on distance of the potential energy of the interaction between two spherically symmetrical particles is often described by a potential of the form

$$V(r) = \frac{\epsilon}{1-6/\alpha}\left\{\frac{6}{\alpha}\exp\left[\alpha\left(1-\frac{r}{r_m}\right)\right]-\left(\frac{r_m}{r}\right)^6\right\}, \qquad (5)$$

where α is a parameter which makes it possible to vary the steepness of the repulsive part of the potential curve, and the significance of ϵ and r_m is clear from Fig. 3. The curve in Fig. 3 is in some cases conveniently divided into two sections — a monotonic section which can be approximated by a function of the form $V(r) = K/r^n$, and corresponds to repulsion (it defines the interaction of particles with kinetic energy $E \gg \epsilon$), and a non-monotonic section — the latter being the region of the minimum on the curve (significant for energies $E \simeq \epsilon$).

From the elementary theory of scattering[20] it is known that for particles of fixed energy the scattering angle χ depends on the impact parameter b (the smallest distance between the centres of the moving particles in the absence of interaction) and the interaction energy for distances close to that of nearest approach of the interacting particles r_0. In contrast to the case of monotonic potentials, the dependence of the angle of deflection χ on the impact parameter for non-monotonic potentials (with a minimum, see Fig. 3) is ambiguous: equal angles χ may correspond to different values of b. A typical dependence in this case is represented by the curve in Fig. 4*a* (this gives the dependence of χ on b^2, which is proportional to the cross-section of scattering at angles greater than χ). The qualitative characteristics of the experimentally observed angular distribution of the scattered particles can be obtained[21] from the curve in Fig. 4*a* by assuming that the number of particles scattered at a given angle is proportional to the quantity $db^2/d\chi = 2\sigma_T \sin\chi$. From the χ–b^2 relationship we can by differentiation readily obtain the dependence of $db^2/d\psi$ on χ (Fig. 4*b*). Although $db^2/d\chi$ and χ in Fig. 4*b* have different signs, the sense of $db^2/d\chi$ is positive, and under the actual

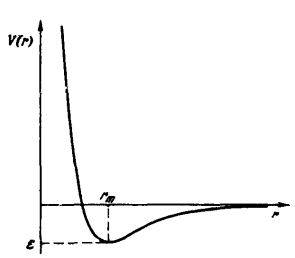

Fig. 3. Typical potential curve for the intermolecular interaction of spherically symmetrical particles.

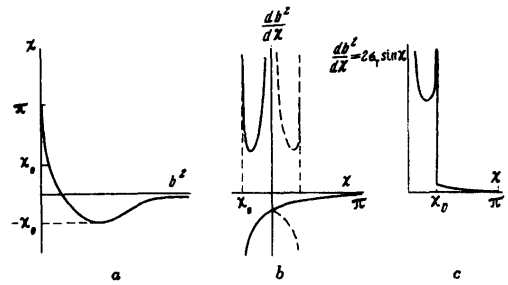

Fig. 4. Construction of the picture of elastic scattering for the interaction described by the potential shown in Fig. 3.

conditions of an experiment it is impossible to distinguish deflections to the right and to the left. Thus the observed scattering picture will correspond to Fig. 4*c*, obtained by transferring the curves (Fig. 4*b*) into the first quadrant, changing the sign, and combining the absolute values of the ordinates of the curves. The right-hand monotonic portion (Fig. 4*c*) corresponds to scattering by the repulsive forces. To study these forces it is most convenient to use the elastic scattering of fast beams of atoms and molecules[22]. Information on these forces is of interest, for example, in connection with the problem of the retardation of fast particles and their transformation into hot atoms.

An extremely useful characteristic of the scattering curve is the emission close to the angle χ_0 (it can be seen from Fig. 4*a* to be linked with the presence of the minimum on the potential curve), which is called the rainbow effect, the angle χ_0 being termed the rainbow angle. The magnitude of this angle, determined by experiment, makes it possible to find unambiguously the depth ϵ of the potential curve (Fig. 3). For non-spherical systems the position of χ_0 depends on the mutual orientation of the molecules. Firsov's discussion[21] was purely classical; quantum-mechanical treatment of this problem[23], without altering the qualitative form of the scattering curve, shifts the position of the rainbow angle slightly to the left of that shown in Fig. 4*c* and smooths out the breaks on the scattering curve. On the basis of the quantitative theory[23] it is now possible to determine from the experimental scattering curves the parameters of the potential curve for the interaction, given in a particular analytical form.

For chemical interaction, analysis of the elastic-scattering picture makes it possible to fix the distortions of the scattering curve produced by chemical effects. The magnitude of this distortion can be used[10] to find the probability of the reaction, defined by the relationship

$$P(\chi, E) = \frac{\sigma_{th}(\chi, E) - \sigma_{exp}(\chi, E)}{\sigma_{th}(\chi, E)},$$

where E and χ are the energy and angle of deflection in the [coordinate] system of the centre of mass, and σ_{th} and σ_{exp} the theoretical and experimental values of the differential cross-section of scattering of molecules with energy E at an angle χ. The value of σ_{th} can be calculated from the known potential or by using the parameters of the interaction potential, found from the initial part of the scattering curve, unperturbed by chemical reaction (Fig. 4*c*), on the assumption that this potential is also applicable to those distances of approach at which chemical reaction is possible. It is thus possible to determine the approach distances corresponding to a probability $P(\chi, E)$ different from zero,

i.e. corresponding to the development of chemical reaction, and also the dependence of P on E. It should, however, be noted that the total reaction cross-sections found from $P(\chi, E)$ are greater by a factor of 5–50 than those calculated from the total product flux. An attempt has been made[24] to analyse the possible reasons for this discrepancy, and it has been shown that the rapid descent observed on the experimental scattering curve in the range of large angles can be explained on the basis of an interaction potential in the form of a curve with two minima (the ordinary van der Waals minimum and a "chemical" minimum).

The elastic-scattering curve observed when two beams intersect can be predicted for a known potential for the intermolecular forces. In the absence of a solution to the corresponding dynamic problem, a picture of the angular scattering of the reaction products cannot be constructed in such simple fashion. Nevertheless, in some cases the laws of the conservation of energy and momentum can be used to predict the form of the distribution. Let us examine qualitatively the scheme for this calculation[25], noting that by varying its parameters (for example the dependence of the reaction cross-section on the energy) until the theoretical and experimental curves coincide, it is possible to determine the values of these parameters. Let us assume first for simplicity that the transformation taking place on collision corresponds to a hypothetical addition reaction A + B → AB, whose probability for one collision is unity (we shall not deal here with the reality of these transformations). In this case it is clear that, as a result of the law of conservation of momentum, after the "adhesion" of the particles, the complex AB in a laboratory system of coordinates will move along the vector of the velocity of the mass centre. Thus the form of the observed angular distribution of the complexes would correspond to the law governing the distribution of the vectors of the rate of movement of the mass centres of the colliding particles, and the magnitude of the beam currents would be determined by the cross-section of collision. The direction of the vector is determined by the rule for combining the particle velocity vectors $\mathbf{v}_A$ and $\mathbf{v}_B$ (Fig. 5*a*), so that the distribution of the velocity vectors of the centres of mass will depend exclusively on the distribution of the magnitudes and directions of the initial velocities of the particles in the intersecting beams. For two collimated beams with uniform velocities, the resulting distribution of the products would be needle-shaped. For collimated beams intersecting at right angles, with Maxwell velocity distribution, the distribution will be bell-shaped (Fig. 5*b*) and related unambiguously (within the limits of the assumptions made) to the bell-shaped form of the Maxwell distribution.

If the beams are poorly collimated, the form of the angular distribution will also be influenced by the scatter of the initial directions of the velocities. Anticipating a little, we may note that the indefinite nature of the interpretation, associated with poor collimation of the beam, reduces slightly the value of the information contained in the angular distribution of the products. In recent work, therefore, considerable attention is paid to the analysis of the perturbations of the elastic-scattering curve resulting from chemical interaction. If reaction does not take place at every collision (for example if the cross-section of the reaction depends on the energy), it is clear that the above bell-shaped distribution of the products will be slightly deformed by this relationship.

For the more real process A + B → C + D the distribution of the products will also depend on the masses of the products and the energy liberated in the reaction. Let us examine the simplest features of the decomposition — the formation of two product particles — in more detail[20], since a quantitative analysis of the internal energy of the products can often be carried out on the basis of only one form of angular distribution of the products.

In the system of the centre of mass, the total momentum of the system A–B is zero, and the scattering in this system will take place in such a way that the total momentum remains unchanged. In the diagram in Fig. 6, the elastic scattering corresponds to rotation of a vector of constant magnitude $\mathbf{v}'_A - \mathbf{v}'_B$, and the ends of the velocity vectors of the scattered particles for different angles of scattering lie on circles A and B with radii $\mathbf{v}'_A$ and $\mathbf{v}'_B$. With inelastic scattering the speeds of the particles of the complex AB, which decomposes in the reaction, depend on the initial kinetic energy and the energy liberated in the reaction, and also on the masses of the products C and D. If all directions of scattering of the reaction products are equally probable (this is characteristic of long-lived complexes), the ends of the velocity vectors of the products will lie on circles C and D (the C-circle is not shown) of the velocity diagram in Fig. 6, with radii $\mathbf{v}'_C$ and $\mathbf{v}'_D$ (in the three-dimensional case these circles will be represented by spheres). The directions of motion of the scattered particles in an l-system (laboratory system of coordinates) are determined by the vectors $C + \mathbf{v}'_C$ and $C + \mathbf{v}'_D$, so that products of type D will be observed within a cone whose generating lines are tangents to the D-circle of the diagram in Fig. 6. From Fig. 6 it can be seen (neglecting possible anisotropy of scattering) that the condition for the creation of a preferential direction in the recording of the products is a low rate of recoil $\mathbf{v}'_D$ compared with the speed of the mass centre of C; otherwise, the distribution will be spread out widely in space. The isotropic nature of the scattering of the products in the c-system (the system

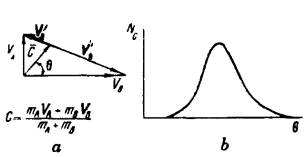

Fig. 5. *a*) Kinematic diagram giving the relationship between velocities in the laboratory coordinate system and the system of the centre of mass; *b*) form of angular distribution of the products.

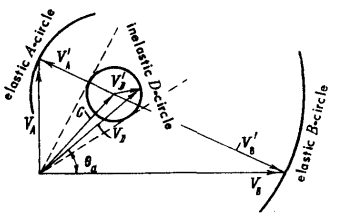

Fig. 6. Kinematic diagram describing qualitatively the main features of the emission of products in the decomposition of the quasi-molecular complex.

of the centre of mass) will be influenced to a marked extent by the lifetime of the complex AB; for schemes with a single simple scattering there should obviously be a preferential direction of scattering for the products.

Returning to Fig. 6, we can see that for isotropic scattering of the products, the compensation of the addition and subtraction of the velocities of recoil from the velocity of the mass centre causes the mean or most probable velocity measured in the l-system to coincide with the latter. For anisotropic decomposition with recoil backwards (relative to $\mathbf{v}'_B$) the velocities in the l-system will be lower than the velocity of the centre of mass, and for recoil forwards they will be higher. Thus by measuring directly the velocities of the product molecules, it is possible to solve the problem of the isotropy of scattering, i.e. the type of reaction mechanism, and also to determine the heat of the reaction $Q = E_1 - E$.

The heat of reaction Q, which is taken to equal the change in the relative kinetic energy, can be expressed

$$Q = \Delta D + \Delta E_{\text{int}},$$

where ΔD is the difference in the energies of bond rupture between reactants and product, and ΔE_{int} the difference in the internal energies of the particles in the initial and the final states. If E is the initial relative energy, the rate of recoil v'_D can be written, from the condition of conservation of energy, in the form

$$v'_D = \left[\frac{2(E+Q)}{M_D(1+M_D/M_C)}\right]^{1/2}.$$

For large positive values of Q, the speed v'_D is high, and the width of the recorded angular distribution of the products will increase considerably; on the other hand, if for a large value of ΔD the experiment reveals a narrow peak in the distribution of the products, this may provide a direct indication of a marked change in the internal energy state of the products ($\Delta D \simeq |\Delta E_{\text{int}}|$).

The value of Q can be effectively decreased only by transfer of part or all of the energy ΔD to internal degrees of freedom of the products. The nature of the angular distribution of the products is more readily used, for quantitative estimation of the fraction of ΔD transferred to internal degrees of freedom, under definite kinematic conditions, in particular for small changes in the reduced mass of the products $\mu_1 = M_C M_D/(M_C + M_D)$ relative to that of the reagents $\mu = M_A M_B/(M_A + M_B)$. In this sense, the reaction K + HBr → KBr + H, which has been studied in most detail, is inconvenient for energetic analysis, since the width of the angular distribution of the products will be strongly influenced not only by Q but also by non-uniformity of the initial velocities. On the other hand, in the reaction $K + CH_3I \rightarrow KI + CH_3$, for example, these two effects are separate because of the displacement of the maximum in the product distribution from the direction of the vector of the most probable velocity of the mass centre and because of the anisotropy of the decomposition itself. The method of kinematic estimation[26] described below in Section III, while clear and effective, was used because of the imperfect nature of the experimental technique employed; it should be noted that machine calculation[27] has revealed considerable ambiguity in these estimations. Direct determination of the velocities of the products using a selector makes it possible to solve the same problem more accurately for any kinematic conditions.

In addition to the above mechanism of adhesion with subsequent isotropic decomposition of the quasi-molecule AB, use is also made of the concepts of ricochet and stripping mechanisms of interaction on collision, taken from the theory of nuclear reactions. In the first case an atom colliding with a molecule as it were ricochets, carrying away an atom from the latter. The characteristic feature of the stripping mechanism is that the colliding atom and the atom removed by it from the molecule move in a direction which coincides with the initial direction of the colliding atom. An important aspect in stripping is that the interaction of the colliding atom with the target atom takes place as though the other atoms in the molecule were not present.

These two mechanisms, unlike the first, are characterised by the existence of a correlation between the directions of the initial and final relative velocities; the products as it were "remember" the initial state. Stripping chemical reactions take place at large impact parameters, so that they have extremely large cross-sections. On the other hand, ricochet collision is possible only when the particles approach close to one another, so that the cross-sections are much smaller than those for stripping.

In this examination no allowance has been made for the angular momentum of the interacting particles. The total angular momentum (orbital plus internal) of the system should be conserved, and this will influence both the angular distribution of the products and the nature of the redistribution of the internal energies, and also the actual probability of the reaction. For reactions in which the orbital momenta of the products and reactants are much greater than the internal momenta, the direction of the relative velocity will be preserved in determining the form of the distribution curve. For a significant change in the reduced mass of the products relative to the original (e.g. a decrease, as in the case of K–HBr), because the total angular momentum is conserved, the initial energy of orbital motion will be converted chiefly into energy of rotational excitation of the products. With increase in the rate of relative motion and hence in the orbital momentum, increase in the rotational excitation of the products may lead for this system to a decrease in the probability of reaction[10]. A complete analysis of the experimental data should therefore include allowance for the influence of angular momentum.

The experimental data obtained correspond to the laboratory system of coordinates, whereas it is more natural to carry out the theoretical analysis in the centre-of-mass system. Interpretation of the data obtained is thus possible if they are converted to the latter system. This problem usually consists of two parts — conversion from the angles giving the position of the detector in the l-system to the angles in the c-system, and conversion of the beam currents measured in the given detector positions into the differential cross-sections. These procedures have been examined in detail elsewhere[28,29].

III. MAIN RESULTS OF THE STUDY OF CHEMICAL REACTIONS IN INTERSECTING BEAMS

To provide a general picture of the results of the study of chemical reactions using intersecting beams, the Table summarises information on studies of this type, with an indication of the extent to which specific reactions have been studied. It can be seen from the Table that most attention has been paid to the study of substitution in HBr, HCl, CH_3I, and HI molecules, and exchange reactions of the type $H_2 + D \rightarrow HD + H$. For a considerable proportion of the reactions given in the Table, the data are scanty, and these reactions will be specially studied in the future.

TABLE.

Reagents	Observed product	Chief results	Remarks	Ref.
K–HBr	KBr	the total reaction cross-section, its dependence on the collision energy, and the threshold energy of the reaction were measured, and the energy state of the reaction products was analysed. The vibrational and rotational energies of the products were determined	the Cs, Rb–HBr systems have been studied	1, 10, 19, 32, 33, 42, 46
K–HCl K–HI	KCl KI	the total cross-section and its dependence on the collision energy were measured, as also the threshold energy of the reaction	data for the K–HCl system were obtained from observations of the elastic scattering	31
K–$C_nH_{2n+1}I$	KI	the total reaction cross-section was estimated (n = 1, 2). Kinematic analysis established that the greater part of the energy of reaction appears as excitation of internal degrees of freedom of the products. Anisotropy in the emission of the products was established. A numerical analysis was made of the dynamics of collision (n = 1, 2)	analogous studies were made with isopropyl, n-propyl, and n-butyl alcohols as reactants	26, 34, 41, 47, 48
K–CH_3Br	KBr	the total cross-section and the threshold of the reaction were determined	data were obtained from observations of elastic scattering	30
K–Br_2 K–I_2 K–ICl K–IBr	KBr KI KCl KBr	the total cross-sections were estimated. It was concluded that the reaction takes place by a stripping mechanism. A kinematic analysis was made of the energy state of the products. The internal energy of the products was measured directly for the K–Br_2 system	analogous results were obtained when K was replaced by Rb or Cs	17, 33, 35, 37, 43, 46, 49, 50
K–CCl_4 K–CH_2I_2	KCl KI	preliminary study indicates the possibility of a stripping mechanism	analogous results were obtained when K was replaced by Cs	17, 43
Rb–SCl_2	RbCl	a stripping mechanism was established for the reaction. Kinematic analysis indicates marked excitation of the reaction products		43
K–$SnCl_4$ K–PBr_3	KCl KBr	preliminary analysis indicates a reaction mechanism intermediate between stripping and complex formation		
H–D_2 D–H_2	HD	the differential reaction cross-sections were estimated. Suggestions were made regarding the mechanism. Numerical calculations of the dynamics of collision were carried out		38–40, 45
N_2^+–D_2	N_2D^+	the total reaction cross-sections were found over a wide range of energies		12
K–SnI_4			distortion of the elastic-scattering curve was noted for the K–SnI_4, $HgBr_2$, HgI_2, and $HgCl_2$ systems. Suggestions were made regarding the possible influence of chemical reactions	44, 51

1. Reactions of the Type K + HX → KX + H

Substitution has been studied in most detail for X = Br; study of this reaction by the molecular beam method was begun as early as 1955.[1] The first results [1] were later refined[10,31], and we shall restrict ourselves to an examination of the later data. Beck et al.[10] studied the chemical interaction accompanying the intersection of a beam of atoms (K) with fixed velocities and a beam of molecules (HBr) with a Maxwell distribution of velocities. The experimental arrangement was similar to that shown in Fig. 2 and the chief results were as follows. (i) The magnitude and nature of the dependence of the total reaction cross-section on the collision energy E were found, and the energy threshold of the reaction was determined. (ii) The data obtained in the study of the elastic scattering were used to determine the dependence of the probability of the reaction on the impact parameter b or the energy of interaction at the distance of closest approach r_0, this energy being related unambiguously to the impact parameter. (iii) A qualitative explanation was obtained for the experimentally observed dependence of the probability of the reaction on the initial collision energy for a fixed value of r_0.

In the discussion of the method used in the theoretical calculation of the angular distribution of the products it was pointed out that this distribution is determined by that of the initial velocity vectors and by the dependence of the reaction cross-section on the relative collision energy.

It might seem that in this experiment, in which the law governing the distribution of velocities in the beams is known, it should be possible, by comparing the theoretical and experimental distribution curves for the products, to determine the unknown energy dependence of the reaction cross-section. It is found in practice, however, that the distribution of the magnitudes and directions of the relative velocities depends not only on temperature but also on the divergence of the HBr beam. The energy dependence of the cross-section is therefore different for different initial assumptions regarding the divergence of the beam. This ambiguity reduces slightly the value of the information associated with the form of the angular distribution; moreover, it provides another illustration of the limitations of methods using a broad spectrum of initial states (in this case relative energies) of the interacting particles. In the work cited[10,31], a different method was selected for determining the required dependence. For different velocities of the beam of K atoms, the measured product current at the maximum was equated to the maximum on the theoretical curve calculated for the divergence which gave the best agreement between experimental and calculated distribution curves. An energy of 2 kcal $mole^{-1}$ was chosen for the normalisation of the calculated and experimental values of the product current.

The final results of the use of this procedure are shown in Fig. 7; here curves A and C correspond to different assumptions regarding the divergency of the beam of HBr

molecules. The experimental points correspond to different measurements and to selection of the most accurate assumption regarding the divergence of the HBr beam. Although the errors in the determination of the energy corresponding to a given value of the cross-section are fairly large, the shape of the curve, even close to the threshold, can be taken as close to curve D (Fig. 7) calculated for the usual solid-sphere model with a threshold energy $E^* = 0.15$ kcal × × mole^{-1}. The exact value of the threshold energy cannot be determined from these data, but it can hardly be greater than 0.4 kcal mole^{-1}. The slightly indefinite nature of the values obtained in this way can be reduced if we utilise for the analysis the results of a study of the elastic scattering of the same partners. The chief features of elastic scattering have been discussed above (Fig. 4), and for complex molecules this discussion is applicable in the approximation corresponding to spherically symmetrical pair interaction.

In the examination of the elastic scattering of reactive particles having a reaction threshold energy E^*, it is possible in principle to compare a certain limiting scattering angle: for large angles of deflection the elastic-scattering curve is distorted as a result of the partial disappearance of HBr molecules by chemical reaction. The experimental scattering curve in the range of angles smaller than the limiting angle can be used to determine the parameters of the interaction potential; from the latter we can then calculate the curve for purely elastic scattering in the range of angles greater than the limiting angle. Theoretical determination of the limiting angle is difficult, and in the work cited[10] it was determined by the *a priori* condition that the probability $P(\chi, E)$ differed from zero; this rather arbitrary choice was justified by the fact that the results obtained showed little dependence on the magnitude of this angle.

From the definition of probability introduced above, the experimental and theoretical scattering curves can be used to find the dependence of $P(\chi, E)$ on the impact parameter or the related energy of interaction for the distance of closest approach $V(r_0)$. Fig. 8 shows the dependence of the probability $P(\chi, E)$ on the energy $V(r_0)$ for five values of the initial energy of the beam of K atoms. In the energy range $0.2 < V(r_0) < 1.2$ kcal mole^{-1}, the probability curves are clearly separated; at higher values of $V(r_0)$ the experimental errors blur this relationship. The asymptotic values of the probability remain less than unity, and this can be taken as an indication that the steric factor is not equal to unity. For the reaction considered, however, it

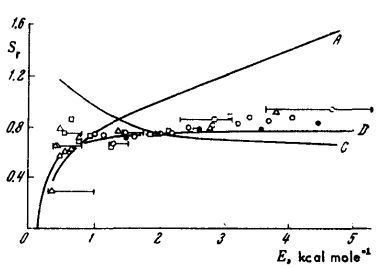

Fig. 7. Experimental dependence of the total cross-section S_r of the reaction K + HBr → KBr + H on the collision energy, and the theoretical curves calculated for various conditions (see text).

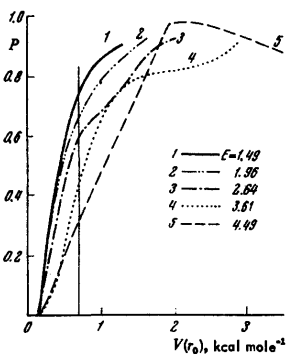

Fig. 8. Experimental dependence of the probability of the reaction K + HBr → KBr + H on the energy of interaction at the point of closest approach for various initial collision energies E.

may be stated that at $b < 2.7$ Å (or for values of $V(r_0) > > 1.2$ kcal mole^{-1}), almost all collisions lead to reaction.

By making use of the expression

$$S_p = 2\pi \int_0^\infty P(\chi, E)\, b\, db = 2\pi \int_0^\pi (\sigma_r - \sigma_s) \sin\chi\, d\chi,$$

we can find the total cross-section of the reaction S_r for a given relative energy E. Comparison of the S_r–E relationship (the solid circles in Fig. 7) with that obtained on the basis of the procedure described above shows good agreement. The absolute values of the cross-sections show less satisfactory agreement, but this can be attributed to the divergence of the beam of HBr molecules. In this way an absolute value of 34 Å^2 is found for the total cross-section of the reaction with an energy of $E = 2.6$ kcal mole^{-1}.

From the results in Fig. 8 it follows that the reaction probability, whose values correspond to the points of intersection of the curves with the normal to the abscissa, decreases with increase in the relative energy for a fixed distance of closest approach r_0. This effect has been interpreted[10] on the basis of the law of conservation of angular momentum. As a result of the marked change in reduced mass ($\mu_1 \ll \mu$), the final orbital momentum is small, and the condition of conservation of total momentum requires a considerable increase in the internal momentum of the KBr molecule. Thus with increase in the initial rate (or relative energy) there is an increase in the internal momentum (and rotational energy) of the KBr molecule, whereas the proportion of the energy corresponding to translational and vibrational degrees of freedom will decrease. It is known from statistical theory that decrease in the phase volume corresponding to these degrees of freedom should lead to a decrease in the probability of reaction. This probability is evidently zero for those initial energies and the orbital momentum for which, as a result of the conservation conditions, the whole of the final energy is equal to the rotational energy. This condition makes it possible, by extrapolation of the data in Fig. 8, to find independently an extremely important parameter (r_m) of the intermolecular interaction potential.

The conservation laws do not permit definite conclusions to be reached regarding the redistribution of the initial kinetic energy and the energy of reaction ΔD. However, direct measurement of the most probable velocities of the

KBr molecules, by means of a velocity selector [32], made it possible to establish fairly precisely how the energy is distributed between the translational and the internal degrees of freedom of the products. This most probable velocity was found, over a wide range of angles of observation, to be slightly greater than the most probable value of C. On the basis of the arguments examined above, this indicates unambiguously that the KBr is emitted predominantly forwards in the c-system (i.e. in the direction of the vector $\mathbf{v}'_K$).

Since the beam of K atoms has a fixed velocity (the beam of HBr molecules has a velocity distribution close to the Maxwell distribution), the geometric locus of the ends of possible velocity vectors of the mass centre will be the normal to the v_K axis at the point $v = m_K V_K/(m_K + m_{HBr})$ (see Fig. 9). When points on this straight line are used to construct circles with radii corresponding to different values of the heat of reaction Q (≥ 0.1 kcal mole^{-1}), the points of intersection of the possible velocity vectors $\mathbf{v}'_{KBr}$ with these circles, for decompositions involving forward emission of the KBr molecules (at an angle of 0° in the c-system), are found to lie on the almost straight vertical lines, corresponding to different values of Q, shown in Fig. 9*b*. The range of possible values of Q is not too great, from -1.85 kcal mole^{-1} for an endothermic reaction with total transfer of the energy to internal degrees of freedom (zero recoil velocity) up to 5 kcal mole^{-1} for the total transfer of the energy of reaction ΔD to the translational energy of the products. We can therefore restrict ourselves to a small number of vertical straight lines (Fig. 9*b* shows only the straight lines for $Q \geq 0$). We can plot on this diagram the measured most probable velocities of the KBr molecules for different angles of observation θ_a, and draw a smooth curve through these points (the values of the probable velocities given earlier [32] have since been slightly corrected [33]). It can then be seen from Fig. 9*b* that this curve intersects the vector of the most probable relative velocity at a point through which the line for $Q = 0.5$ kcal mole^{-1} also passes; hence the most probable exothermic heat of reaction is ~ 0.5 kcal mole^{-1}, and almost all the energy of reaction is used up in internal excitation of the products (the reaction can be regarded as thermoneutral). It has thus been possible to confirm by direct experiment the long-discussed assumption that reactions involving alkali-metal atoms and halogens lead to transfer of the greater part of the energy of reaction into internal degrees of freedom.

The reactions for substituents X = Cl (slightly endothermic reaction) or I were studied by Ackerman et al. [31] on the assembly described by Beck et al. [10] The total cross-sections of the reactions for $E = 2$ kcal mole^{-1} were found to be 28 Å^2 for K–HI and 3.9 Å^2 for K–HCl.

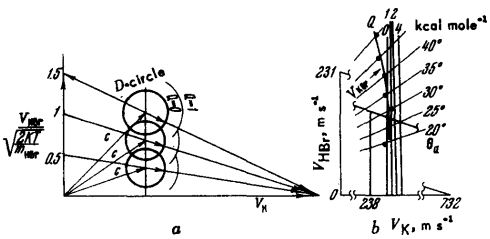

Fig. 9. Kinematic scale diagram for determining the internal energy of the products of the reaction K + HBr → KBr + H.

A method analogous to that described above was used to find the dependence of the probability of reaction on $V(r_0)$, the interaction energy at the point of closest approach. For the K–HCl system the threshold value $V_n(r_0) = 0.55 \pm \pm 0.1$ kcal mole^{-1} was clearly fixed. The plot of this dependence shows two additional breaks. Since their positions are given by the expression $V_n(r_0) + v(\hbar\nu)$, they may be due to the formation of products in different vibrational states ($v = 1$ and 2). For the K–HI system the behaviour of the probability function is quite different: it shows a sharp ascent beginning from a threshold energy $V_n(r_0) = 0.2$ kcal × × mole^{-1}, after which there is no dependence on $V(r_0)$ and only a weak dependence on E. No significant energy dependence of the total reaction cross-section has been found for either system.

2. Reactions of the Type K + $C_nH_{2n+1}I$ → KI + C_nH_{2n+1}.

Reactions of this type, unlike those examined above, are characterised by a comparatively small change in the reduced mass. This feature makes it possible, even for two beams which do not have fixed velocities, to make a quantitative analysis of the energies of the products and to establish anisotropy in their emission. A typical picture of the angular distribution of the products for the K–CH_3I system is shown in Fig. 10 (the curves correspond to two different experiments and the broken line gives the calculated curve). A rough estimate of the total cross-section of reaction gives for the K–CH_3I system the value 35 Å^2. Variation of the source temperature for the beam of K atoms indicated [26] that the activation energy of this reaction is small and does not exceed 0.3 kcal mole^{-1}.

Detailed kinematic analysis of the K–CH_3I system [26] gives interesting results. For a molecule of the product KI, the recoil velocity in the c-system may have different directions and magnitudes determined by the relationship

$$v'_{KI} = \left[\frac{M_{CH_3}}{M_{KI}}\,\frac{2(E+Q)}{M_{KI}+M_{CH_3}}\right]^{1/2}.$$

The ends of the possible recoil velocity vectors in the planar case (Fig. 10) lie on circles with radius v'_{KI}. In the scale diagram in Fig. 10 these circles are shown for various values of Q up to 25 kcal mole^{-1} (the difference in the energies of rupture of the C–I and K–I bonds). It can be seen from Fig. 10 that large values of Q (>5) correspond to recoil velocities close to or greater than the velocity of the centre

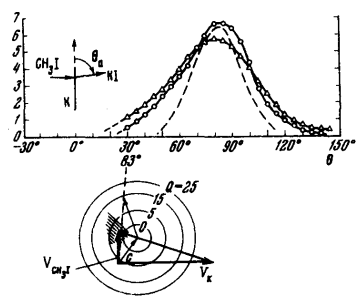

Fig. 10. Angular distribution of the products of the reaction K + CH_3I → KI + CH_3 and kinematic diagram explaining the marked internal excitation of the products.

of mass C. Thus, whereas for $Q = 0$ the range of possible appearance angles of KI lies between 40° and 70°, we find that for $Q = 6$ kcal mole^{-1} KI can be observed for any angle in the l-system. It can thus be seen from the diagram that the observed maximum in the product current for the angle $\theta_a = 83°$ in the l-system can be attributed only to the result of anisotropic emission with recoil of KI molecules backwards ("ricochet"), i.e. in the opposite direction to the velocity of the K atoms (in the c-system). When allowance is made for the cylindrical symmetry of the emission with respect to the relative velocity vector (Fig. 10), it is found that the observed current in the region of the maximum yield of products can be realised only for values of Q not exceeding 5 kcal mole^{-1}, so that ~ 80% of the energy of reaction is used up in excitation of the products.

A more accurate estimate is possible when a mechanical selector is used. Analogous results are also obtained when the number of carbon atoms $n = 2$, and also when K atoms are replaced by Cs or Rb.[26] For systems containing propyl or butyl groups it was found that the radical group has no steric influence (equal reaction cross-sections) and that the final kinetic energy of the products decreases with increase in the mass of the radical group.

For reactions involving alkyl halides, a comparison has recently been made of the calculated (by means of an electronic computer) and experimental angular distributions of the reaction products. Support has been obtained for the qualitative conclusions and quantitative estimations discussed above, but it follows from the calculations that the experimental data can be described satisfactorily with a slightly greater scatter in the values of Q and χ than appeared earlier. This ambiguity is associated with the absence of velocity selection[34].

Study of the K–CH_3Br system[30] using a beam of K atoms of fixed velocity shows that the dependence of P on E for a fixed value of r_0 is opposite to that observed for the K–HBr system (Fig. 9). The reaction probability P does not exceed 0.8, and increases sharply from 0 to this value at a threshold energy $V_n(r_0) = 0.25$ kcal mole^{-1}.

3. Reactions of the Type $X_2 + A \rightarrow XA + X$

The reactions of this type which have been studied, with X = halogen and A = alkali-metal atom are given in the Table. For the Cs–Br_2 system, the elastic-scattering curve does not show a rainbow peak, and the curve descends rapidly even in the range of relatively small angles; these distortions of the scattering curve clearly indicate a high value for the reaction cross-section[35]. In contrast to the systems examined earlier, comparison of the forms of the calculated and experimental curves for the angular distribution of the products shows considerable divergence: in particular, there is a marked difference in the positions of the maxima on these curves. This lack of agreement can be eliminated by making the theoretical calculation on the assumption that the Cs atom interacts only with one Br atom and that the bond between the atoms in the molecule can be neglected (impulse approximation). This impulse scheme corresponds to abandonment of the model which assumes the formation of a complex or composite molecule. As usual, the spectrum of possible recoil velocities of the products is determined by the heat of reaction and the initial energy E; estimates[35] show that, if the final kinetic energy is, for example, $2.2E$, the reaction products are "smeared" over a solid angle of 4π. Since the experiments revealed a narrow distribution peak at $\theta_a = 8$, it must be concluded that not more than 0.5–1 kcal mole^{-1} is transferred to the translational energy of the products and that all the remaining available energy (~ 99% of ΔD) is used up in internal excitation of the CsBr.

The agreement between the experimental curve and the results of the calculation according to the impulse mechanism also leads to the conclusion that this reaction corresponds to the class of reactions of the stripping type. Indications of this mechanism were obtained for analogous systems[36] using beams of K, Rb, and Cs and of Br_2, I_2, ICl, and IBr which did not have fixed velocities. Estimation of the total reaction cross-section for these systems leads to values of the order of 100 Å^2. For these systems the reactions are strongly exothermic (ΔD = 40–50 kcal × × mole^{-1}), but the final kinetic energy of the greater part of the products (in the region of the intensity peak), e.g. in reactions involving Br_2 and I_2 molecules, does not exceed ~ 1 kcal mole^{-1}. Thus the products have a high vibrational excitation (the rotational energy is restricted by the conservation of angular momentum). Direct measurements of the velocities of the products using a selector, carried out recently[33,37] for the K–Br_2 system, show that the spectrum of internal energies of the KBr molecules is extremely broad, extending from 4 to 17 kcal mole^{-1}. Moreover, it may be concluded from the experimental results that the angular distribution of the products in the c-system corresponds to their emission forwards within a cone having an angle of divergence of ~ 30°.

Marked internal excitation of the products takes place also with the Cs–ICl and Cs–IBr systems; here, in the estimation of the vibrational excitation, allowance must be made also for the possibility of reactions leading to products of the type CsI or CsCl (the detector will not distinguish, for example, CsI and CsBr molecules). The high reaction cross-sections and the predominant emission of the products forwards (in the direction of motion of the alkali-metal atom) in these systems again indicates that the reaction takes place by a stripping mechanism.

4. The Reactions $H_2 + D \rightarrow HD + H$ and $D_2 + H \rightarrow HD + D$

Even the first results of a study of these reactions are of considerable interest[38,39], in connection with the possibility of comparing the experimental data with theoretical analysis. The most detailed information was obtained by Datz and Taylor[38], who compared theoretical and experimental angular distribution curves for the products HD (Fig. 11). The section of the curve shown by the broken line in Fig. 11 corresponds to extrapolation of the experimental points into the range, inaccessible to measurement, of the "shadow" of the beam of D, containing a small but significant quantity of HD, The calculated angular distribution of the velocity vectors of the centres of mass is shown by the solid curve and the points correspond to different experiments.

The slight (10–15°) symmetrical broadening of the experimental curve in comparison with the theoretical curve (Fig. 11) can be explained in two ways. It may result either from formation of a short-lived linear complex or from strong excitation of the molecules of the products. A scheme of phase detection[38] makes it possible to estimate the times of flight or the velocities of the HD molecules; this estimate is incompatible with the second possibility, so that there is greater justification for the assumption that a short-lived

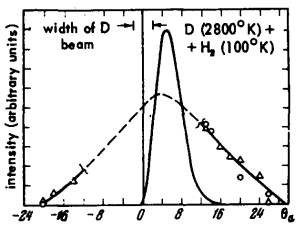

Fig. 11. Angular distribution of the products of the isotopic substitution $H_2 + D \rightarrow HD + H$ (the broken line gives the extrapolation of the experimental points and the solid curve gives the results of the theoretical calculation).

complex is formed, leading to the appearance of non-excited products. The experimental data for these reactions are as yet scanty and unreliable, but numerical analysis of the dynamics of the collisions of the D and H_2 molecules [40] also shows that for this system the direct-interaction scheme is preferable to the collision-complex model.

5. Numerical Methods

To conclude this review of experimental studies of chemical interaction in intersecting beams with thermal velocities, we must consider another extremely promising approach which makes use of fast computers for model calculations on elementary reactions. This approach is of interest in two respects: firstly, it reveals certain details of the mechanism of a chemical transformation inaccessible to present-day experimental technique and shows possible directions for subsequent experiments; and secondly, it will supplement the semi-empirical method for determining potential-energy surfaces.

Numerical methods have been used [40,41] to analyse the dynamics of collisions leading to the reactions $CH_3I + K \rightarrow$ $\rightarrow KI + CH_3$ and $H_2 + D \rightarrow HD + H$. The method involves essentially direct integration of the equations of motion for the approaching atoms and molecules, i.e. exact calculation of the classical trajectories of motion of three or more atoms. By tracing the trajectories of individual parties with time, it is possuble to pick out those which correspond to the appearance of a new combined state and hence determine the reaction cross-section. By varying the parameters of the calculation, we can find the most favourable conditions for the reaction. In the specific case of the $K-CH_3I$ system, the calculations are simplified by assuming that the methyl group behaves approximately as a separate structureless particle with the same mass, the potential of whose interaction with the I atom is the same as that for CH_3. The classical collision trajectories of these partners are computed for different initial conditions, and the familiar Monte Carlo method is used to obtain results averaged over the real distributions of the impact parameters, orientations, and vibration phases [45]. Experiments with intersecting beams permit direct comparison with the results of the calculations, and if correspondence is observed for some results, it maybe expected that other theoretical results, which cannot be directly compared with experimental data (because the latter are not available), are also applicable. On the other hand, by comparing the corresponding results of calculations and experiments and subsequently achieving better agreement, we can readily refine the form of the potential-energy surface.

One may ask to what extent we are justified in describing the motion of atoms in a chemical interaction by classical equations of motion. A number of factors indicate that this is possible — the large masses of the particles, the adiabatic nature of the chemical transformation, the many-quantum nature of the process of bond rupture in the original molecule and of bond formation in the product molecule, etc.

The quantum-mechanical treatment of elementary chemical processes is at present in its early stages. This, together with the considerable mathematical difficulties encountered in the quantum calculations, forces us to use a classical treatment in those cases where it is justified. In the final analysis, justification for the classical description must be provided by agreement between experimental data and calculations.

In particular, for the $K-CH_3I$ system [41], numerical calculation leads to agreement between the available data and makes it possible to find the lifetime of the complexes formed in a collision, their configuration, and a number of other relevant details. An interesting conclusion, following from the results of experiments and calculations on the dynamics of the collisions for the simplest reacting systems (e.g. $K-CH_3I$ and H_2-D), is that the reaction takes place in a short time interval, corresponding to the transit time in the interaction range. Numerical calculations have not as yet given any indication of the formation of the quasi-molecular complexes (albeit short-lived) used in the transition-state theory.

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The above discussion leads to the following conclusions.

Use of the molecular beam method to study elementary chemical reactions (and also processes of energy exchange for internal degrees of freedom and interaction with a solid surface) gives valuable information on important details of reaction mechanisms.

The intensive development of experimental technique is leading to a continuous increase in the volume of information which can be obtained in experiments with molecular beams. We now have the real possibility of controlling not only the initial state of the reagents — the molecules of the intersecting beams — but also the final energy state of the reaction products. Further extension of these studies is possible by making use of the latest achievements in the production of intense beams with electron-volt energies and methods for their detection.

The possibility of using this method to study the internal energy state of reaction products is of intrinsic value in connection with the problem of stimulated radiation.

Comparison of experimental data with numerical calculations of the dynamics of collisions accompanied by chemical transformation may give information on the properties of potential-energy surfaces and supplement the semi-empirical method for their determination. The numerical method also makes it possible to reveal a number of details of the chemical interaction which cannot be determined experimentally (the lifetime of the complex, its configuration, etc.) and stimulates the organisation of new experiments to detect the effects predicted by the calculation.

The study of reactions accompanying the intersection of beams whose molecules have been excited beforehand is of considerable interest. These studies are most conveniently carried out by the molecular beam method.

The results obtained up to the present and the observed general trend towards an extension of these studies indicate the need for the rapid introduction and extensive utilisation of this method in the appropriate research organisations of the Soviet Union.

A number of papers [47-58] on the subject of this review have been published since the present manuscript was submitted.

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THE ELECTROCHEMICAL PROPERTIES OF MOLYBDENUM AND TUNGSTEN

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Molybdenum and tungsten find widespread application in the manufacture of high-grade steels, electrical engineering electroplating, and other fields. These metals play an important part in improving processes of chemical technology, where they are employed as catalysts. Their compounds will probably also find application in semiconductor technology. The preparation of the metals in an extremely pure state therefore acquires great significance. Electrochemical methods occupy a prominent place in solving this problem. At the same time, it becomes necessary to determine traces of molybdenum and tungsten in various materials and industrial products. Electrochemical methods of analysis have an important role in this connection also.

A systematic account of the large amount of published information which has accumulated on the electrochemistry of molybdenum and tungsten will considerably ease the labour of researach workers in this field.

1. POTENTIALS OF REDOX SYSTEMS

The peculiar structure of the electron shells of molybdenum and tungsten is responsible for the variety of types of compounds, in which the metals exhibit a valency varying from two to six. Compounds with hydrogen, which are so typical of elements of the sulphur subgroup, are unknown with molybdenum and tungsten[1]. These metals form a series of redox systems, characterised by definite potentials. Owing, however, to the instability of several compounds in aqueous solution, the redox potentials of these systems have not been evaluated. In particular, no data have been published for the systems M^{V}/M^{IV}, M^{IV}/M^{III}, and M^{III}/M^{II} in aqueous solution. Quadrivalent compounds of molybdenum and tungsten are extremely unstable in aqueous solution, undergoing disproportionation with the formation of trebly charged and quintuply charged ions.

The potentials of other redox systems have been studied quite thoroughly. Thermodynamic calculations of potentials yield the values[2,3]

Mo^{III}/Mo_{solid} – 0.20 V; Mo^{V}/Mo^{III} ~ 0.0 V;

WO_4^{2-}/W_{solid} ~ –1.1 V; W^{III}/W_{solid} > –0.05 V;

WO_3/W^{III} < –0.05 V; WO_3/WO^{3+} + 0.26 V.

Careful measurements of the potentials of various systems containing molybdenum were made by Foerster and his coworkers[4], a selection of whose results is given in Table 1.

Table 1 shows the potential of the Mo^{VI}/Mo^{V} system depends on the relative concentrations of oxidised and reduced forms. This relationship should be consistent with the formula

$$\varphi = \varphi_0 + 0.058 \log \frac{[M^{VI}]\,[H^+]^2}{[M^{V}]}, \quad (1)$$

in conformity with the potential-determining process

$$MO_2Cl_3^- + 2H^+ + 2Cl^- + e \rightarrow MOCl_5^{2-} + H_2O. \quad (2)$$

The measured potentials differ somewhat from those calculated theoretically by means of Eqn. (1). The theoretical shift in potential produced by doubling the hydrochloric acid concentration should be $0.058 \times 2 \log 2 = 0.035$ V. The changes in potential found experimentally on passing from 2 *N* to 4 *N* and 8 *N* HCl were respectively 0.039 V and 0.190 V. The potentials of this system in 4 *N* and 8 *N* HCl should be +0.628 V and +0.663 V.

The discrepancy between theoretical and experimental values was attributed partly to variation in the activity of hydrochloric acid with change in its concentration. On the other hand, these workers postulated the formation of more stable chloride complexes of quinquevalent molybdenum, which would have inevitably produced a positive shift in the potential with increase in concentration of the chloride ion.

The normal oxidation potential of this system was found to be +0.400 V.[3] The material of the indicator electrode (platinum, iridium, gold) had practically no effect on the potential.

The potential of the Mo^{V}/Mo^{III} system was calculated by means of the equation

$$\varphi = \varphi_0 + 0.029 \log \frac{[Mo^{V}]\,[H^+]^2}{[Mo^{III}]}, \quad (3)$$

in conformity with the reaction

$$MoO^{3+} + 2H^+ + 2e \rightleftarrows Mo^{3+} + H_2O. \quad (4)$$

The data in Table 2 show that the potentials of this system are more negative than those of the previous system. The

TABLE 1. Potentials (on standard hydrogen scale) of the Mo^{VI}/Mo^{V} system in hydrochloric-acid solutions.

Mo^{VI}/Mo^{V} ratio	Acid concn., *N*	Potential Pt, V
99:1	8	+0.822
99:1	4	+0.632
99:1	2	+0.593
97:3	2	+0.576
50:50	2	+0.532
3:97	2	+0.484
1:99	2	+0.470

TABLE 2. Potentials (on standard hydrogen scale) of the Mo^{V}/Mo^{III} system in hydrochloric-acid solutions.

Mo^{V}/Mo^{III} ratio	Acid concn., N	Potential Pt, V
97:3	8	+0.322
97:3	4	+0.258
97:3	2	+0.188
50:50	2	+0.114
3:97	2	+0.054
1:9	2	+0.054

same features were observed in the variation of the potential with the concentration ratio of oxidised and reduced forms, and also with the concentration of hydrochloric acid.

Doubling the hydrochloric acid concentration should produce a shift in potential of $0.029 \times 2 \log 2 = 0.017$ V. For a concentration ratio of 100 between oxidised and reduced forms, the corresponding potentials should be +0.205 V (4 N HCl) and +0.232 V (8 N HCl). The measured values were more positive, +0.258 and +0.322 V. Thus the changes in potential accompanying increase in concentration of hydrochloric acid considerably exceeded the theoretical values.

The redox potentials of systems involving molybdenum had been measured by Chilesotti[5] before Foerster's investigations. The measurements were made in the titration of tervalent molybdenum with potassium permanganate. The results obtained by the two workers differ considerably.

The Mo^{VI}/Mo^{V} system has been studied also by other workers[6,7], who explained the variation in potential with the concentration of hydrochloric acid not only by the influence of the hydrogen-ion concentration but also by the occurrence of two different forms of quinquevalent molybdenum.

Syrokomskii studied the potentials of redox systems as functions of the concentrations of complexing agents[8,9]. He showed the effect of the concentration of the anions PO_4^{3-}, $C_2O_4^{2-}$, and $C_4H_4O_6^{2-}$ on the potential, which becomes more negative on addition of the complexing agent. The shift in potential produced by the different anions varies in the above sequence.

The effect of thiocyanate on the redox potential of the Mo^{VI}/Mo^{V} system was studied by Tarayan and Ekimyan[10], who found that the potential becomes more positive with increase in the thiocyanate concentration.

The potential of the W^{VI}/W^{V} system was first measured by Collenberg and Guthe[11], who obtained a value of +0.26 V, differing from that calculated by means of Eqn. (1). The experimental results have been reproduced by Chernikhov and Goryushina[12,13] in the potentiometric titration of sexivalent tungsten with bivalent chromium. Some lack of reproducibility in the potentials of systems containing quinquevalent tungsten has been explained by its rapid oxidation in air. According to some workers[14], however, solutions of quinquevalent tungsten are stable, and can be employed as working solutions in oxidimetric titration. A systematic study of the redox potentials of tungsten systems in hydrochloric acid solutions has been made by Geyer and Henze[15,16], some of whose results are listed in Table 3.

Tungsten was obtained in lower states of oxidation by electrolysis with platinum, mercury, and amalgamated

TABLE 3. Potentials (on standard hydrogen scale) of redox systems in hydrochloric-acid solutions.

W^{VI}/W^{V} ratio	Potential, V		W^{V}/W^{III} ratio	Potential, V	
	12.5	8.0		12.5	9.5
90:10	+0.42	+0.29	90:10	+0.13	+0.03
50:50	+0.36	+0.20	50:50	+0.05	−0.03
10:90	+0.37	+0.16	10:90	−0.02	−0.11

lead electrodes. With a platinum electrode (at a cathodic current density of 0.01–0.3 A cm^{-2}) quinquevalent tungsten was obtained. A sharp jump in potential occurred only when the quinquevalent state was reached. The subsequent conversion of W^{V} into W^{III} was not accompanied by a sharp change in potential. In phosphate solutions reduction occurred with difficulty to quinquevalent tungsten.

In contrast to molybdenum, the potential of the W^{V}/W^{III} system was calculated on the basis of

$$2WOCl_6^{2-} + 4H^+ + 4e \rightleftarrows W_2Cl_9^{3-} + 2H_2O + Cl^-, \quad (5)$$

as the potential-determining process. Consequently the equation

$$\varphi = \varphi_0 + 0{,}029 \log \frac{[W^V][H^+]^4}{[W_2Cl_9^{3-}]}, \quad (6)$$

was used for the calculations.

It is evident from Eqn. (6) that variation in the hydrogen-ion concentration should have a more marked effect on the potential than in the case of the analogous molybdenum system. Measurements of potential for these systems containing different concentrations of hydrochloric acid show that the potential shifts to more positive values with increase in the hydrogen-ion concentration, but no exact relationship is observed. The potentials of both systems are affected by the concentration ratio of oxidised to reduced forms.

Nevertheless, the total concentration of oxidised and reduced forms has hardly any effect on the potential. Addition of phosphoric acid makes the potential more negative[17]. Oxalic acid and other organic complexing agents have the opposite effect. The potentials of the redox systems were not studied in alkaline solutions owing to hydrolysis of the salts with the formation of precipitates. However, the potential of the $W(CN)_8^{3-}/W(CN)_8^{4-}$ system was measured in the presence of potassium cyanide, and found to be +0.57 V. Several authors regard the presence of W^{IV} in these solutions as certain[2,18].

Methods for the oxidimetric determination of molybdenum and tungsten have been developed on the basis of potential measurements in redox systems containing these elements[12,13,19–27].

The potential of metallic molybdenum in solutions of various electrolytes has been measured by Akimov[28], Shatalov[29], and others. A characteristic feature of Akimov's results (Table 4) is their dependence on the previous mechanical treatment of the electrode surface: an electrode having an uncleaned surface shows far more positive potentials than does an electrode which has first been cleaned. This indicates the presence of oxide films on the electrode surface.

The influence of the nature of the electrolyte on the potential is most probably linked in some way with the formation of oxide films. In conformity with this, the potentials are more positive in acid than in alkaline solutions

(dissolution of the film). With time the potential in an alkaline solution becomes more positive, obviously owing to the accumulation of alkali-insoluble oxidation products of molybdenum.

Shatalov[29] considers the concentration of hydrogen ions to be the main potential-determining factor in the case of molybdenum. Potential measurements over the pH range 1–8 have shown a linear relation, which can be expressed by the empirical formula

$$\varphi = \frac{0.35}{0.40} - 0.045\,\mathrm{pH}.$$

Table 5 gives results obtained by Shatalov[29] for the dependence of the potential on the nature of the anion. The results resemble those in Table 4. Chloride and hydroxide ions exert the greatest depolarising effect on molybdenum.

Kruger and Kahlenberg[30] have studied the potentials of molybdenum in solutions of various electrolytes saturated with inert gases (Table 6). It is difficult to compare Table 6 with Table 5 because of differences in the electrolyte concentrations. However, comparison of certain data (for KOH and HCl) indicates considerable negative shifts in potential when a solution is saturated with an inert gas. The reason for these shifts is obscure.

A similar variation in the potential with the nature and concentration of the anion has been obtained by several workers for tungsten[28,29,31-33], results of Korner[31] and Shatalov[29] being listed in Tables 7 and 8 respectively. Table 7 shows the depolarising action of anions on the potential. In the presence of chloride, bromide, iodide, and cyanide ions the potential becomes more negative. A considerable negative shift in the potential is observed also in ammoniacal and alkaline solutions. Shatalov's results (Table 8), obtained for tungsten in the same solutions, differ somewhat from those of Korner. The difference is most probably explained by some irreproducibility in the surface state of the tungsten electrode.

The dependence of the tungsten potential on the pH of the solution was studied by Holven[34]. In view of the direct interdependence of these properties, tungsten was recommended as an indicator electrode for the determination of pH[35].

TABLE 4. Potentials (V, on standard hydrogen scale) of metallic molybdenum in electrolyte solutions.

3% NaCl			0.1 *N* HCl		
1 min	5 min	cleaned	1 min	5 min	cleaned
+0.103	+0.080	−0.362	+0.338	+0.318	−0.072
0.1% *N* HNO_3			0.1 *N* NaOH		
1 min	5 min	cleaned	1 min	5 min	cleaned
+0.349	+0.323	−0.022	−0.326	−0.242	−0.602

TABLE 5. Potentials (V, on standard hydrogen scale) of metallic molybdenum in solutions of various electrolytes.

Electrolyte concn.	Potential
3% NaCl	+0.105 * −0.362 **
0.1 *N* HCl	+0.330 * −0.092 **
0.1 *N* HNO_3	+0.329 * −0.019 **
0.1 *N* NaOH	−0.228 * −0.660 **
1.0 *N* HCl	+0.372 * +0.305 **
1.0 *N* KOH	−0.320 * −0.400 **

* After 5 min.
** Cleaned.

TABLE 6. Potentials (V, on standard hydrogen scale) of molybdenum in electrolyte solutions saturated with inert gases.

Gas	Electrolyte	Potential
N_2	KCl	−0.246
	KOH	−0.695
	HCl	+0.085
H_2	HCl	−0.228
	KOH	−0.680
	HCl	+0.094
Ar	KCl	−0.245
	KOH	−0.680
	HCl	+0.080
He	KCl	−0.250
	KOH	−0.645
	HCl	+0.074

TABLE 7. Potentials (V, on standard hydrogen scale) of tungsten in electrolyte solutions.

Electrolyte	Potential
H_2SO_4	+0.193
HCl	+0.256
HNO_3	+0.311
KOH	−0.315
NaOH	−0.316
NH_4OH	−0.238
KCN	−0.647
KF	+0.522
KCl	+0 563
KBr	+0.589
KI	+0.733
KNO_3	+0.300
K_2SO_4	+0.719

TABLE 8. Potentials (V, on standard hydrogen scale), of tungsten in electrolyte solutions.

Electrolyte	Potential	Atmosphere	Electrolyte	Potential
HCl	+0.345	H_2	KI	+0.170
	+0.305	N_2	H_2SO_4	+0.193
	+0.311		KCl	0.00
HNO_3	−0.370	H_2	KF	−0.045
KOH	−0.320	N_2	NH_4OH	−0.238

2. COMPOSITION AND SPECTROPHOTOMETRY OF COMPLEX COMPOUNDS

A vast literature exists[36-76] on the composition of compounds formed by sexivalent molybdenum and tungsten with inorganic and organic reagents. The composition is greatly

dependent on the nature and concentration of the ligand. Thus the compound $H_2Mo_4O_{13}$ is assumed[36] to be present in dilute hydrochloric acid solutions. With increasing concentration of the acid, the cationic form $HMo_2O_6^+$ is produced. Further increase in the concentration of hydrochloric acid to 5–6 *N* promotes formation of the complex MoO_2Cl_2 by the reaction

$$HMo_2O_5^+ + 3H^+ + 4Cl^- \rightarrow 2MoO_2Cl_2 + 2H_2O.$$

The formulae WCl_6, $WOCl_4$, and WO_2Cl_2 have been attributed[11,77] to the chloride complexes of sexivalent tungsten. In aqueous solution the complexes are unstable, undergoing hydrolysis to form a precipitate of tunstic acid. The chloride complexes of sexivalent molybdenum and tungsten have their maximum light absorption in the ultraviolet. The complex $H^+[MoO_3.H_2SO_4]$ can be formed in sulphuric-acid solution.

Numerous heteropolyacids of molybdenum and tungsten are known, and a fair amount of information has been published[37-39, 50-53] on their composition and structure. The composition of the heteropolycompounds is represented by the general formula $H_3[El^1(M_3O_{10})_4]nH_2O$ or $H_4[El^2(M_3O_{10})_4].nH_2O$, where El^1 = P, As, Sb, etc. and El^2 = Si, Ge, Sn, etc.

Sexivalent molybdenum and tungsten form many complex compounds with organic reagents. Some of these are brightly coloured, and are used for the absorptiometric determination of molybdenum. In several cases the composition of the compounds which are formed has not been established[40-48, 54-76].

The chloride complexes of quinquevalent tungsten possess a blue colour and their maximum absorption lies in the range 600–700 nm. These compounds, and the corresponding molybdenum derivatives, are stable to the action of atmospheric oxygen[78]. The composition of the chloride complexes of quinquevalent tungsten has not been adequately studied[79-81].

In contrast to W^V, the chloride complexes of Mo^V exist in two forms — monomeric (> 7 *N* HCl) and dimeric (< < 2.5 *N* HCl) — which coexist in equilibrium in the intermediate range (2.5–7 *N* HCl).[46,78,82-87] However, as Babko points out[82], the composition of the chloride complexes of Mo^V and their equilibrium conditions have not been established at concentrations of hydrochloric acid of 3–6 *N*. The compounds $M_2[MoOCl_5]$, where M is an alkali metal, have been isolated from solutions of concentrated hydrochloric acid. According to this author[82], quinquevalent molybdenum does not form stable chloride complexes in solutions of dilute hydrochloric acid, but is most probably present as the cation MoO_2^+. As the concentration of hydrochloric acid increases, the cation MoO^{3+} is formed:

$$MoO_2^+ + 2H^+ \rightleftarrows MoO^{3+} + H_2O.$$

Further increase in the concentration of the acid results in the formation of the complexes $MoOCl^{2+}$, $MoOCl_2^+$, and $MoOCl_3$.

Many investigations have been made of the conditions of formation and the composition of the thiocyanate complexes of molybdenum and tungsten[88-127]. Several workers assume that the thiocyanate complex of tungsten is represented by the formula $W(CNS)_5$, while other results indicate that the tungsten is tervalent[121], the formula of the complex being WOCNS. Maximum light absorption occurs at 400 nm. Contradictory views are held on the valency of molybdenum in the thiocyanate complex: Maas[90] and Krauskopf[91] state that molybdenum is tervalent in such compounds, Markle[93] regards it as quadrivalent, and finally Sand[92] considers it to be quinquevalent. Babko's investigations[94,95], together with those of other workers[99], indicate that molybdenum is quinquevalent in this compound, whose composition corresponds to the formula $Mo(CNS)_5$ (λ_{max} = 420 nm).

There are indications of the existence of halide complexes of quadrivalent tungsten and molybdenum[128] having the formulae MCl_4, $MBrCl_3$, etc., which are unstable in aqueous solution.

The halide complexes of tervalent tungsten[129] and molybdenum[130-133] have been studied the most thoroughly. Various authors state that tervalent molybdenum exists in two forms — green and red — in hydrochloric-acid solution. The green form is produced in dilute hydrochloric acid. Some workers have therefore assumed that it corresponds to the cation Mo^{3+} or MoO^+, and that the red form, which is present in concentrated solutions of hydrochloric acid, represents the anion $MoCl_6^{3-}$. Other workers[131] regard the occurrence of two forms of tervalent molybdenum as due to *cis–trans* isomerism of a complex having the same composition $MoOCl.4H_2O$ or $[MoCl_2(H_2O)_4]^+$.

The green form is unstable, being converted into the red form by increasing the acidity or raising the temperature. A characteristic property of tervalent molybdenum is its comparatively ready oxidation by hydrogen ions to yield quinquevalent molybdenum. As a consequence, aqueous solutions of tervalent molybdenum are unstable. Spectrophotometry of the solutions confirms the presence of two forms: the $D-\lambda$ curves exhibit two absorption maxima, at 420 and 520 nm (7 *N* HCl).[132,133]. Dilution of the solution results in a shift in the maximum to shorter wavelengths, which corresponds to a change in composition of the complexes, with the ultimate formation of tervalent molybdenum hydroxide.

The chloride complexes of tervalent tungsten also exist as two forms — $H_5W_3Cl_{14}$ and $H_3W_2Cl_9$ — with absorption maxima in the region of 515 and 462 nm (red and yellow respectively). According to other workers[129], however, the occurrence of two forms of tervalent tungsten is due, as in the case of molybdenum, to *cis–trans* isomerism.

Tungsten and molybdenum blues constitute a peculiar group of compounds[134-139], whose exact composition has not been established.

3. ELECTROLYSIS OF SOLUTIONS

The first work on the electrolytic reduction of sexivalent molybdenum was done by Gahn[140]. This work was qualitative in character, as were investigations by other workers[141-145]. In particular Grotthus[141], who reduced sexivalent molybdenum in sulphuric-acid solution, noted the appearance of blue oxides of molybdenum on the cathode, metallic molybdenum not being isolated. The first attempt to isolate metallic molybdenum by electrolysis with a mercury cathode was made by Férée[146], who used a current density of 5 A cm^{-2} in the cold. The reduced molybdenum dissolved in the mercury to form an amalgam. Later Meyer[147,148] obtained molybdenum amalgam by the electrolysis of sulphuric-acid solutions. This work was repeated by Russell[149] and by Bock[150], who found the optimum conditions

(1–1.5 N H_2SO_4, cathodic c.d. 0.6 A cm^{-2}) for the quantitative deposition of molybdenum. Electrolysis with a mercury cathode was used for the quantitative separation of molybdenum from several elements which do not form amalgams. Electrolysis with solid cathodes, on the other hand, proved useful for the quantitative isolation of molybdenum as the oxide Mo_2O_3 [151,152] with subsequent quantitative determination.

Detailed investigations of the electrolytic reduction of sexivalent molybdenum were made by Chilesotti[5,130,153] and by Foerster[4,154], who studied the effect of several factors — the material of the electrode, the nature and concentration of the electrolyte, the current density, etc.

Chilesotti's results showed that the current efficiency is close to 100% at not very high current densities (0.047 A cm^{-2}), but it falls considerably with increase in current density. The variation in current efficiency with the concentration of hydrochloric acid is irregular: the efficiency decreases on passing from 9N to 6N HCl, and then increases again on passing to more dilute solutions of the acid. The time variation in the current efficiency shows considerable irregular fluctuations. The initial decrease in efficiency is most probably associated with the formation of insoluble products on the mercury surface, which lower the hydrogen overpotential. Chilesotti explained the subsequent rise in the curve by the formation of molybdenum amalgam. The process was accelerated by raising the temperature, the current efficiency being increased. The maximum current efficiency was observed on a lead electrode; values of the same order were obtained on mercury and platinum electrodes.

Chilesotti regarded the high current efficiency on lead as possibly due to the discharge of lead ions which had passed into solution under the influence of an oxidant (molybdenum). During electrolysis with platinum, mercury, and iridium cathodes, the cathode potential became more negative, reaching 0.40 V. No change in potential was observed on tin and lead cathodes.

It follows from the above survey that metallic molybdenum was not deposited when solutions were electrolysed with solid electrodes. However, a series of papers have shown that metallic molybdenum can be deposited in the presence of added iron, nickel, or cobalt salts[155–161]. The additives are usually regarded as depolarising the discharge of Mo^{VI} by forming an alloy on the cathode. Furthermore, the hydrogen overpotential on the alloy is greater than that on pure molybdenum, which also favours the process. According to Ernest and Holt[161], the mechanism of the electrode reaction is

$$M^{2+} + 2e \rightarrow M^{\circ},$$
$$MoO_4^{2-} + 4H_2O + ne \rightarrow Mo(OH)_{6-n} + (2+n)\,OH^-,$$
$$Mo(OH)_{6-n} + (6-n)\,H + M \rightarrow MMo + (6-n)\,H_2O,$$

where n = 1–3. This scheme is seen to involve the participation of atomic hydrogen in the reduction of Mo^{VI}.

Many workers have investigated the electrolytic reduction of W^{VI}. One of the first papers on the electrolysis of tungsten[162] contains a brief mention of the possibility of obtaining an amalgam by electrolysing acid solutions of tungstates containing hydrofluoric acid. This possibility has been confirmed in later work[163]. Leiser[163] made a systematic investigation of the electrolytic reduction of W^{VI} with platinum and lead cathodes, nickel being used as anode. In all cases sparingly soluble blue products were formed, whose composition could not be established. The current efficiency was low, not exceeding 3%.

A broad investigation was made by Rosenheim[164], who used phosphoric, arsenic, and organic acids ($H_2C_2O_4$, $H_2C_4H_4O_6$) as complexing agents. Lead, platinum, mercury, and zinc were examined as cathodes. Reduction took place in stages. From the colour changes occurring in the solution (blue, brown, cerise), this worker concluded that quinquevalent, quadrivalent, and tervalent tungsten was formed. Neither changing the current density nor varying the temperature resulted in further reduction. Collenberg[165,166] showed that, when a mercury cathode was used, the current efficiency did not exceed 24%, and fell sharply with time. It increased slightly with decrease in the current density. Reduction took place at negative values of the cathode potential. Thus at a current density of 0.016 A cm^{-2} the initial potential was -0.70 V, and at 0.004 A cm^{-2} it was close to zero.

Tervalent tungsten was obtained as the final product of reduction on mercury, lead, and tin cathodes. The current efficiency was far smaller on a mercury cathode than on lead.

Rosenheim suggested the following mechanism of reduction

$$\left.\begin{aligned} W^{VI} + e &\rightarrow W^{V} \\ W^{V} + 2e &\rightarrow W^{III} \\ W^{V} + e &\rightarrow W^{IV} \end{aligned}\right\}.$$

On a platinum cathode the final reduction product is merely quinquevalent tungsten.

It must be noted that molybdenum and tungsten redox systems, although reversible in the equilibrium state, are appreciably polarised during electrolytic reduction[154,169]. This is presumably due to the formation of insoluble films on the electrode surface.

Neumann and Richter[167] investigated cyanide solutions of tungsten, and attempted to deposit the metal on a mercury cathode, but were unsuccessful. However, Jackson et al.[168] confirmed Feree's preparation[162] of tungsten amalgam, and pointed out that no acid other than hydrofluoric should be present in the solution. The optimum acid concentration was 4.6 N HF, and the current density 0.60–1 A cm^{-2}.

As with molybdenum, metallic tungsten is not deposited from aqueous solution on solid cathodes. However, it has been deposited from solutions in organic solvents[170,171].

The need for tungsten coatings of high corrosion resistance led to comprehensive investigations of the conditions for the deposition of metallic tungsten from aqueous solution. The problem was first solved by Fink[172]. The tungsten deposits obtained were dense, bright, and stable to the action not only of hydrochloric and sulphuric acids but even of nitric acid. Holt[173] proposed an alkaline electrolyte for this purpose. In the cold a deposit of tungsten oxides was obtained from an alkaline solution. At 85° the cathode became covered with a silver-white film of metallic tungsten. The current efficiency was ~ 1%, which diminished with increase in current density, the optimum value of which was 0.1 A cm^{-2}. Phosphate solutions also were useful for the deposition of metallic tungsten, but the weight of the deposit did not exceed 0.0077 g.

Holt showed[174-176] that metallic tungsten can be deposited from aqueous solution only if the solution contains traces of iron (0.001 g per 75 ml of solution). The cathode deposit contains up to 35% of iron. The quality of the cathode deposit is equally affected by raising or lowering the concentration of iron in the solution: in both cases oxides of varying composition, not metallic tungsten, are deposited.

Nickel, cobalt, and copper have also been proposed[177-179] as impurities promoting the deposition of metallic tungsten. The tungsten content of the cathode deposit did not exceed 50%. In later work Holt[180] has examined aluminium, beryllium, zinc, manganese, tin, cadmium, etc. as additives, and other workers[181-185] have also investigated this problem.

The mechanism by which the additives exert their effect has not yet been elucidated. Various views have been expressed[180,186-188].

1. The discharge of W^{VI} involves two alternating processes at the cathode:

$$(a)\ M^{n+} + 2e \rightarrow M^{\circ},$$
$$(b)\ WO_4^{2-} + 8H^+ + 6e \rightarrow W^{\circ} + H_2O.$$

Reaction (*a*) continues until the surface is completely covered with a thin layer of the impurity metal, which then catalyses the discharge of W^{VI} ions, reaction (*a*) giving way to reaction (*b*). Thus the processes alternate. The hydrogen overpotential is lower on the pure metals (iron, cobalt, nickel) than on their alloys with tungsten.[180,186,188,189].

2. An alloy is formed by the discharge of mixed complexes of tungsten with the impurity metal. Holt[186] used a polarographic method to test this hypothesis. He found that the half-wave potential of the second reduction wave of nickel (-2.02 V) is displaced to more positive values (-1.67 V) in the presence of tungsten. In his opinion this indicates the discharge of a mixed complex of nickel and tungsten.

3. A layer of impurity metal deposited on the cathode promotes formation of an active form of hydrogen, which reduces the W^{VI}. The theory that several compounds are hydrogenated by atomic hydrogen formed on the cathode surface is supported by Kobozev[190-193]. It has been shown[194] that tungsten trioxide placed a short distance from the cathode surface acquires a blue colour as a result of its reduction by atomic hydrogen emitted from the mercury surface. However, Bagotskii and Iofa state[195] that the trioxide is not reduced when not in immediate contact with the cathode, which they explain by the direct reduction of WO_3 to W_2O_5:

$$2WO_3 + 2H^+ + 2e \rightarrow W_2O_5 + H_2O.$$

4. Depolarisation of the discharge of W^{VI} is due to the formation of an alloy of tungsten with the impurity metal, a view supported by Solov'eva and Vagramyan[187], who reject the theory that the metals are deposited layer by layer. If this did occur, fluctuations should be observed in the cathode potential, but these are not in fact observed.

The electrolytic oxidation of tungsten passes through the stage of formation WO_2, W_2O_5, and WO_3.[196,197]

Several papers have appeared[198-200] on the electrolysis of non-aqueous solutions and of melts of tungsten salts, but these fall outside the scope of the present review.

4. REDUCTION WITH METALS AND AMALGAMS

Reducing agents of various strengths have been used for the non-electrolytic reduction of sexivalent molybdenum[201-223] and tungsten[224-253]. Such electronegative metals as lead, cadmium, and zinc were used as reducing agents in the early work. Reduction with zinc was first employed by Pisani[201] and by Pfordten[224]. This method has subsequently been tried by a number of investigators[202,203,211,225-231].

Tervalent molybdenum and tungsten were obtained as the final products. Reduction involved the successive formation of quadrivalent and quinquevalent molybdenum and tungsten. Some workers did not achieve a definite degree of reduction[203-205].

More recently[206,207] metallic aluminium has been used as reductant. According to Riegel and Schwartz[206] reduction in 2 *N* HCl or 1.25 M H_2SO_4 solution first yields orange quinquevalent molybdenum and then green tervalent molybdenum. When this work was checked[207], it was actually found that reduction extended only to the quinquevalent state. However, further reduction is achieved by adding a tin(II) salt. The mechanism of the process was assumed[207] to be

$$Mo^{VI} + Sn^{II} \rightarrow Mo^{IV} + Sn^{IV}, \quad (1)$$

$$Mo^{IV} \rightarrow Mo^{V} + Mo^{III}, \quad (2)$$

$$Mo^{V} + Sn^{II} \rightarrow \begin{matrix} Mo^{III} + Sn^{IV} \\ Mo^{IV} \end{matrix}. \quad (3)$$

Reaction (3) takes place after Mo^{VI} has been completely converted into Mo^{V}.

Electropositive metals such as silver and mercury have also been studied[208-212] as reducing agents, reductors filled with the freshly deposited metals being used. Furman[212] observed the quantitative conversion of sexivalent into tervalent molybdenum in solutions in concentrated hydrochloric acid. In more dilute (1.5–3.5 *N*) acid only quinquevalent molybdenum was formed. Silver had a similar effect. Holtje and Geyer[205] found results for the reduction of molybdenum(VI) by mercury and silver to be reproducible and reliable. Reduction of W^{VI} with silver and mercury in concentrated hydrochloric acid[248-250] yields W^{V}. A method based on preliminary reduction of Mo^{VI} and W^{VI} with silver has been used for the quantitative determination of molybdenum and tungsten in iron–molybdenum, iron–tungsten, and iron–molybdenum–tungsten alloys[253].

Someya's work[217,232,236] was based on the use of liquid amalgams as reducing agents, and during subsequent years many workers have studied the reduction of Mo^{VI} and W^{VI} with amalgams[213-223,233-235,237-252].

Bismuth amalgam reduces Mo^{VI} to the tervalent or the quinquevalent state depending on the acidity of the solution[217]. Sexivalent tungsten is reduced to W^{V} only in concentrated hydrochloric acid.

The amalgams of lead, tin, cadmium, and zinc reduce molybdenum and tungsten quantitatively to the tervalent state[223,234]. According to other workers, however, quadrivalent tungsten is formed on reduction with cadmium amalgam[235] and with metallic cadmium[17]. The reduction of tungsten is prevented by the presence of phosphates and fluorides[237]. Different authors have divergent opinions on the degree of reduction of W^{VI} by lead amalgam. Thus

Someya[236], Holt[237], Babko[238], and Vlasak[239] state that at 60° lead amalgam converts W^{VI} into W^{III}. According to Polotebnova[240], however, lead reduces W^{VI} to W^{IV}. The lack of agreement among the results may be due to differences in the temperature conditions.

Most authors tend to regard the method based on preliminary reduction of tungsten followed by oxidimetric titration as unsuitable for quantitative purposes. Nevertheless, the method has recently been applied to the analysis of steel[245].

Work has been done on the reduction of W^{VI} by lead, zinc, and sodium amalgams in non-aqueous solution[247]. Zinc amalgam effects complete reduction to W^{III}, lead amalgam to W^{IV}, and sodium amalgam reduces W^{VI} incompletely to W^{IV}.

5. POLAROGRAPHY

Several papers have been published on the polarographic reduction of molybdenum[254-291] and tungsten[292-312] at a dropping mercury cathode. The first work in this field was done by Uhl[254], who effected reduction in nitric-acid solutions, using lactic and oxalic acids as complexing agents. The Mo^{VI} polarograms comprised two waves having half-wave potentials of -0.35 and -0.50 V (relative to the saturated calomel electrode, s.c.e.). The proportionality of the height of the first wave to the concentration of molybdenum formed the basis of a method for the quantitative determination of molybdenum and phosphorus. Stern[255] applied Uhl's method to the analysis of biological materials, and obtained two waves with half-wave potentials of -0.40 and -1.20 V. A well defined pH dependence of the wave heights was observed. The wave height is strictly proportional to the molybdenum concentration only within a narrow range of the latter[256], and hence the polarographic determination of molybdenum with nitric acid as supporting electrolyte is not very promising. According to Gokhshtein[257] the reduction of molybdenum in nitric-acid solution is complicated by polymerisation phenomena. He suggested phosphoric acid as supporting electrolyte for the polarographic determination of molybdenum.

Stackelberg et al.[258] found that sharp molybdenum waves are obtained in sulphuric acid, whose concentration should be a least 18 *N*. Molybdenum gives one wave with a potential of -0.26 V. The wave height is proportional to the molybdenum concentration, which also permits the method to be used for quantitative analysis[259]. A detailed investigation of the process occurring in aqueous sulphuric acid has been made by Kolthoff[260].

As Stackelberg points out[258], the molybdenum reduction wave appears also in aqueous hydrochloric acid. According to him, however, it corresponds to the reduction not of molybdenum but of mercuric chloride resulting from the oxidation of metallic mercury by molybdic acid.

Kanevskii and Shvartsburd[261] obtained cathodic waves of Mo^{VI} in 88–90 vol.% phosphoric acid. A method was worked out for determining molybdenum in ores containing 0.005–50%.

Molybdophosphoric heteropolyacid undergoes reduction in phosphoric acid solution. The polarography of heteropolyacids of molybdenum — molybdosilicic, molybdogermanic, etc. acids — has formed the subject of several recent papers. Grasshoff and Hahn[262-265] state that, when these acids are reduced at a dropping mercury cathode, tervalent and quinquevalent molybdenum is formed. They find that the wave heights depend on the acid concentration.

A few papers have been published on the polarography of the lower states of oxidation of molybdenum. In particular, Deshmukh[266] has studied the reduction of quinquevalent molybdenum, a solution of which he obtained by reduction with hydrazine. The polarogram obtained with sulphuric acid as supporting electrolyte consisted of two waves, which he regarded as due to stepwise reduction to quadrivalent and tervalent molybdenum. The half-wave potentials are greatly dependent on the acidity of the solution, becoming more positive with increasing acidity.

Meits[267] obtained polarograms in a citrate buffer solution. Sexivalent molybdenum gives a single wave with a half-wave potential of -0.927 V. Tungsten is not reduced under these conditions, so that the method can be used for the quantitative determination of molybdenum in the presence of tungsten. This worker assumes that reduction involves the formation of quadrivalent molybdenum. Parry and Yakubik[268] consider that polarographic reduction in tartrate solutions yields tervalent and quinquevalent molybdenum. A similar opinion is held by Pecsok and Parkhurst[269]. Pantani[270] has made a polarographic investigation of the citrate, oxalate, and tartrate complexes.

Complexone III has also been proposed as complexing agent[271-273], and it masks the interfering effect of tungsten. Ammonium fluoride has been proposed for a similar purpose[274].

Sinyakova and Glinkina[275] obtained two Mo^{VI} reduction waves (with half-wave potentials of -0.27 V and -0.73 V) using acetic acid as supporting electrolyte. With increasing concentration of the acid, the second wave disappears, while the half-wave potential of the first wave becomes more positive. Two sharp waves are obtained also in a solution containing Complexone III. The half-wave potentials depend on the pH. The reduction of molybdenum takes place also in neutral medium (ammonium oxalate), but the shape of the wave depends on the concentration of the supporting electrolyte[276].

With mixed supporting electrolytes ($HCl + HClO_4$, $HCl + H_2O_2$) catalytic polarographic currents have been observed. Thus Jones[277], while reducing Mo^{VI} with a supporting electrolyte comprising 0.75 M H_2SO_4 + 1 M $HClO_4$, observed a catalytic wave due to reoxidation of tervalent to quadrivalent molybdenum by the perchloric acid, the half-wave potential being -0.21 V.

Holten[278] used this supporting electrolyte for the quantitative determination of molybdenum in minerals and ores. The method proved convenient in the analysis of titanium alloys[279]. Tungsten does not interfere with the determination.

The catalytic reaction in perchloric-acid solutions has been studied by Rechnitz and Laitinen[280], who found that the rate of the process depends on several factors, in particular on the concentrations of molybdenum and perchloric acid.

Sinyakova and Glinkina[281] explained the appearance of a catalytic current in solutions of perchloric acid containing Mo^{VI} by the reoxidation of quadrivalent to quinquevalent molybdenum by the perchloric acid. To confirm this hypothesis they recorded polarograms of molybdenum which had been prepared by reducing sexivalent molybdenum by iron(II) sulphate, with perchloric acid as supporiing electrolyte. The polarogram comprised one wave having a

half-wave potential corresponding to the second Mo^{VI} wave in the same supporting electrolyte. Tervalent molybdenum gave a small wave having a more negative half-wave potential‡.

Haight[282-284] also believes that quadrivalent molybdenum catalyses the reduction of perchloric acid. Catalytic currents representing the reduction of perchlorates and nitrates are used for the polarographic determination of molybdenum[285,286].

Kolthoff and Parry[287] obtained catalytic currents with $HCl-H_2O_2$ supporting electrolytes. The current was proportional to the concentration of Mo^{VI} and hydrogen peroxide. According to these workers, the MoO_4^{2-} ion forms a peroxo-compound MoO_5^{2-}, which is then reduced at the dropping mercury cathode to MoO_4^{2-}:

$$MoO_5^{2-} + 2H^+ + 2e \rightarrow MoO_4^{2-} + H_2O.$$

Vlček[288] assumes that the Mo^{VI} polarographic currents in concentrated sulphuric-acid solution are also catalytic in character, being due to reoxidation of Mo^{V} to Mo^{VI} by the sulphuric acid.

In addition to the acid and neutral supporting electrolytes mentioned above, those of basic character have also been suggested[289] for the reduction of molybdenum.

Polarography has been used to study the composition of the citrate, tartrate, and phosphate complexes of molybdenum, with perchloric and nitric acids as supporting electrolytes[290]. Thus various supporting electrolytes have been used in studying the polarographic reduction of Mo^{VI} in order to find conditions which are of practical convenience for its quantitative determination.

In several of these papers suggestions have been made concerning the mechanism of the process. However, different authors hold contradictory views on this topic, which suggests that insufficient study has been made of the polarographic reduction of molybdenum[291]. This applies equally to catalytic processes.

Little study has been made of the mechanism of the electrolytic reduction of molybdenum with a large mercury cathode and its reduction by amalgams.

Relatively little work has been done on the polarographic reduction of tungsten. Stackelberg[292] found that W^{VI} is not reduced at a dropping mercury cathode in neutral and alkaline solutions, whereas in concentrated hydrochloric-acid solutions it gives a wave having a half-wave potential of -0.42 V. A sharp wave appears also in the presence of phosphoric acid. This workers does not indicate the degree of reduction of the tungsten to which this process corresponds.

Lingane and Small[293] made a detailed investigation of the polarographic reduction of W^{VI} in concentrated hydrochloric acid. The degree of reduction of the tungsten was determined coulometrically or by titration with potassium iodate solution. They also used electrolysis with a mercury cathode at a controlled potential to elucidate the mechanism of the process. The individual forms of reduced tungsten were identified spectrophotometrically. These workers found that in 12 *N* HCl the tungsten(VI) gives two waves, the first beginning at zero applied e.m.f., and the second wave having a half-wave potential of -0.56 V (s.c.e.). In less concentrated solutions the potential of the second wave becomes more negative. From the ratio of the constants for the diffusion currents of first and second waves it was concluded[293] that reduction extends to the quinquevalent and tervalent states respectively. The coulometric measurements at the corresponding potentials (-0.40 and -0.67 V) and titration with iodate support this view.

Laitinen et al.[294] studied the polarographic behaviour of W^{VI} in hydrochloric-acid solutions containing perchloric acid and lithium chloride. The half-wave potential and the number of electrons involved in the reaction were determined from the slope of the linear plot of $\log [i/(id - i)]$ against the electrode potential. These workers consider[294] that quinquevalent and tervalent tungsten is formed during the polarographic process. However, they do not exclude the possibility of the formation of quadrivalent tungsten, since the reverse process passes through this stage. A catalytic current due to reduction of the perchlorate ion was observed on a portion of the first wave in these solutions. Laitinen and Ziegler[295] explained the appearance of the catalytic current by reoxidation of the quinquevalent tungsten ion, formed during polarography, by perchloric acid. The catalytic current is large, and depends not only on the concentration of W^{VI} but also on the concentrations of hydrochloric and perchloric acids. A catalytic current has been observed also in the polarography of solutions containing hydrogen peroxide. Kolthoff and Parry[287] established that the magnitude of the catalytic current depends on the concentrations of tungsten(VI), hydrogen peroxide, and acid. The maximum catalytic current was observed in sulphuric-acid solution. These workers tend to think that the variation in the catalytic current with change in acid concentration is due to different degrees of polymerisation of the tungsten(VI).

The catalytic current is suppressed by the presence of complexing agents in the solution, and this effect has been used to determine the composition of the oxalate complexes[296].

Souchay[297,298] studied the polarographic reduction of sexivalent tungsten in solutions of various inorganic complexing agents (PO_4^{3-}, AsO_4^{3-}, GeO_3^{2-}, SeO_3^{2-}, BO_3^{3-}, etc.). Other authors have discussed the mechanism of this process[299,300].

Souchay[301] has recently studied the polarographic reduction of metatungstates in aqueous hydrochloric and sulphuric acids. Electrolysis using a mercury cathode, combined with spectrophotometry, suggests a stepwise reduction of W^{VI} to W^{V} and W^{III} in concentrated acid solutions. In dilute solutions of the acids three or more waves appear. The half-wave potentials and the wave heights depend on the acid concentration. Souchay attributes this to different degrees of polymerisation of the metatungstate and hence to variation in the number of electrons taken up by each molecule, which he regards as fluctuating between 21 and 36.

A polarographic method has been used in several investigations to determine the composition of complexes[302,303]. According to Pantani and Desideri[304] W^{VI} gives a well defined wave in solutions of phosphoric acid ($> 4\,N$). In dilute solutions the polarograms consist of three or more waves. These workers assume that reduction extends to

‡ The method employed by these workers is incorrect: (1) they do not exclude the effect if iron and cadmium on the polarograms; and (2) mixing Mo^{III} with perchloric acid before polarography should result in the instantaneous oxidation of the former by the ClO_4^- ions. An intermediate reduction product of perchloric acid, chlorine, will then appear in the solution.

the quinquevalent state. The occurrence of more than one wave, however, they attribute to variation in the diffusion coefficient of large complex molecules with increase in the acid concentration.

Two waves are present in the reduction of sexivalent tungsten from hydrochloric-acid solutions containing ammonium thiocyanate, their appearance being explained by successive reduction of the chloride and the thiocyanate complexes[305].

In the presence of organic complexing agents (oxalic, tartaric, citric acids, etc.), too, W^{VI} is reduced at a dropping mercury electrode in acid solutions[306-310]. The wave heights vary with the acid concentration. The optimum pH depends on the nature of the complexing agent.

A method based on the use of concentrated hydrochloric acid as supporting electrolyte has been recommended for the analysis of steels, alloys, etc.[292,311,312].

The published information shows that the mechanism of the polarographic reduction of sexivalent molybdenum and tungsten has not yet been thoroughly elucidated. Therefore no indication is given in reference works as to the degree of reduction of tungsten. The point is reflected in the treatise by Krykova et al.[291]

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APPLICATION OF SYNTHETIC ZEOLITES (MOLECULAR SIEVES) TO CATALYSIS

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I. INTRODUCTION

Natural crystalline aluminosilicates (zeolites, molecular sieves) were shown in 1915 to have catalytic properties.

Catalysts for cracking, oxidation, and other reactions (both inorganic and organic), based on these materials, were subsequently patented [1], but initially they did not find wide practical use.

Advances in the field of zeolite synthesis, mainly in the period 1940–1950, have revealed new potentialities for these materials. Dozens of zeolites with enhanced adsorption properties and thermal stability were prepared, including some which have no natural counterpart. The production of types A and X synthetic zeolites on a semi-industrial scale [2] began in 1954: since then, these zeolites have achieved wide popularity as sorbents for drying, purification, and separation [3,4]. However, their catalytic properties have been very little studied [5], in spite of their great potential importance, which arises from the striking specificity of their properties, making possible the solution of many practical and theoretical problems in catalysis. The combination of a well-defined crystalline structure with uniform pores of molecular dimensions enables highly selective catalysts to be prepared [6–8]. By using zeolites with orifices (leading to voids within the crystals) of the correct size, we can localise reactions on the outer surface of the catalyst and eliminate the influence of internal diffusion. The aluminium in crystalline alumina–silica zeolites always has tetrahedral coordination. (This applies to the cationic forms: three-coordinated aluminium is also present in decationated modifications.) The excess negative charge of the aluminium–silicon–oxygen skeleton is compensated by cations of different elements (when first synthesised, zeolites are usually in the sodium form). These cations can be exchanged for equivalent amounts of other cations, giving rise to various ion-exchanged modifications with a range of different catalytic properties. Multifunctional multicomponent catalysts, obtained by introducing various catalytically active components into the voids of zeolites, have enhanced stability, arising either from hindered migration of the metal or from some kind of compound formation through the orifices of molecular dimensions [9] by which the voids are interconnected.

By virtue of their high chemical stability (particularly in organic media), and of their thermal stability, zeolites can be used at high temperatures, and are easily regenerated. In this respect they are superior to organic cationic ion-exchange resins, whose thermal stability is still limited [10] to 160–190°, whereas zeolites are stable up to 800° and above.

In recent years, zeolites in which some of the AlO_4 and SiO_4 tetrahedra are replaced by structural units containing Ge, Ga, Be, Mg, Cr, and other elements have been synthesised by isomorphous substitution. A comparison of the catalytic properties of these zeolites with those of the corresponding cationic forms of alumina–silica zeolites will provide valuable evidence on the relative contributions of the cationic and the anionic parts (sites) of the zeolites to their catalytic activity, and will reveal new ways of varying and controlling the properties of zeolite catalysts.

Research carried out during the past few years has led to the development of new, highly active catalysts, some of which have already found industrial application, whilst others are undergoing trials. The following new industrial catalysts — Durabead 5, a cracking catalyst almost 100 times as active as amorphous alumina–silica catalysts, the cracking catalyst [11] XZ-15, and also the isomerisation catalyst MB-5390 (SK-100) for n-alkanes, showing enhanced stability towards water and sulphur, and enabling reactions to proceed at temperatures 60–80 deg lower than existing bifunctional catalysts of the metal–acidic oxide type [12] — have been developed in the USA. In addition to their high activity and selectivity, these catalysts are remarkably stable towards impurities in the crude materials, particularly sulphur and nitrogen compounds, and heavy metals, which usually poison catalysts of other types.

These special features of zeolite catalysts are their most promising characteristics, and are the reason for the increasing scientific and practical interest in these materials.

II. GENERAL INFORMATION ON ZEOLITES, AND ON SOME OF THEIR PHYSICOCHEMICAL PROPERTIES

Most of the synthetic zeolites, like all natural zeolites, are aluminosilicates†. These compounds can have a fibrous structure, a layer structure, or a three-dimensional (skeletal) structure. Zeolites with a layer structure are thermally unstable, and possess only moderate adsorption properties. The most valuable crystalline alumina–silica zeolites from the point of view of adsorption and catalysis are those with a stable three-dimensional skeleton, and the following discussion will be mainly confined to zeolites of this type.

Approximately forty natural zeolites have been described so far, but the total number of synthetic zeolites exceeds fifty [18]. The most interesting of these are the zeolites of types A, X, Y, L, S, P, E, mordenite, and others. Their general empirical formula can be written

$$M_{2/n}O \cdot Al_2O_3 \cdot x\,SiO_2 \cdot y\,H_2O,$$

where n is the valency of the metal cation M, while x is the SiO_2/Al_2O_3 molar ratio, and y is the number of moles of water. The value of x determines the structure and the properties of the zeolites. Thus, in a type A zeolite x is close to 2.0, in a type X zeolite it varies from 2.2 to 3.0, in a type Y zeolite from 3.1 to 5.0 [18] (or to 6.0 according to other workers [8]), and in a synthetic mordenite values as high as 10 have been reported [19–21]. The zeolite lattice consists of SiO_4 and AlO_4 tetrahedra. As we have already pointed out, the aluminium–oxygen and silicon–oxygen tetrahedra in zeolites can be replaced by tetrahedra of other ions, e.g. P^{5+}, Ga^{3+}, $Ge^{4\pm}$, etc. These tetrahedra arrange themselves so as to form polyhedra. Thus, 8 tetrahedra can form a cube, 12 can form a hexagonal prism, and 24 can form a cubic octahedron. The unit cells of the zeolites are formed by the packing of these polyhedra. Voids appear between and within the polyhedra: these are interconnected by oxygen rings (orifices). The cross-sectional areas of these voids (pores) and orifices are of molecular dimensions, and are strictly constant for each type of zeolite. This property of zeolites accounts for their exceptionally high selectivity in adsorption and catalytic processes: whether or not the voids within the crystal are accessible to adsorbed molecules

† Zeolites in which aluminium has been replaced by gallium [13,14] or chromium [15,16], and the silicon by germanium [13], beryllium, or magnesium [17], have been synthesised and investigated. Their importance from the point of view of catalysis will be discussed below.

depends on the size of the latter (critical diameter). The sizes of the large voids and of their interconnecting orifices are set out in Table 1 for various zeolite samples. More detailed discussions of zeolite structure[3,4,22-30] and of the critical diameters of molecules[22] have been published.

The adsorption properties of zeolites become apparent only after dehydration, because the voids in the crystals are filled with water molecules during preparation. Zeolitic water can be removed from the crystals by heating to 300–350°, which does not affect the crystal lattice structure of most zeolites. The ease of dehydration depends on the ion-exchange form of the zeolite. Thus, the calcium form is considerably more resistant to dehydration than is the sodium form[29]. However, zeolites retain small amounts of water even after treatment at 500°. Table 2 lists the water losses reported[31] for some zeolites on heating from 500° to 1000°.

After dehydration, zeolites have a high adsorption capacity. The combined volume of the voids can amount to 50% of the total volume of the crystals[23]. An important property of the zeolite lattice is its high thermal stability. Thus, NaA zeolite is stable up to 700°, and NaX up to 750–800°. The thermal stability of zeolites increases with increasing silicon content[32], and for samples of a given type it is strongly dependent on the nature of the cation, increasing with the radius of the latter[33,34]. As noted above, the cations which compensate the negative charges of the AlO_4^- tetrahedra can undergo ion exchange. The character of the exchange process is determined by the nature, size, and charge of the cations, and by the structure type of the zeolite[35-41]. Cation exchange takes place most effectively in an alkaline medium[42]. Large cations show an ion-sieve effect, which affects the extent and the rate of exchange[35,36,43]. The long-range order of the zeolite crystal lattice is sometimes disrupted by cation exchange. This effect is very sensitive to the pH of the solution in which the exchange is taking place: many zeolites, such as types A and X, lose their structure in acid media (below pH 5). The stability of the structure is also a function of the extent of ion exchange.

The presence of mobile cations in zeolites gives rise to electrical conductivity[23,44,45], the activation energies for conduction and the resistivities being less than in other types of crystal.

TABLE 1. Diameters of large voids and of their interconnecting orifices in some zeolites.

Zeolite	LiA	NaA	KA	CaA	NaX (NaY)	CaX (CaY)	CaM*	H–M
Diameter of large void, Å	12	11–12	11	11	11–13	11–13	7**	7
Size of orifices, Å	4.4	4.0	3.3	5.0	~9	~8	4	6.6

* CaM and H–M are the calcium and the hydrogen forms of synthetic mordenite.

** Length of large channel.

TABLE 2. Thermogravimetry of some zeolites.

Zeolite	NaX	MgX	NaY	MgY	CaY	SrY	BaY
Degree of exchange, %	—	70	—	72	72	77	77
Water lost on heating from 500° to 1000°, wt. %	0.27	1.04	0.14	0.88	0.88	0.45	0.25

As well as the various cationic forms, the hydrogen and the decationated forms of molecular sieves are of great importance in catalysis. These modifications have a high catalytic activity[19-21,46], are more stable towards acids than the cationic forms[47], and show some other specific properties. Replacement of a cation by a proton by ion exchange in an acid medium is possible only with high-silica zeolites, such as mordenite[27]: most other zeolites decompose under these conditions. Barrer suggested the use of the ammonium form[48], which undergoes a reaction giving rise to the H-zeolite when heated in oxygen:

$$4(-O^- \ldots NH_4^+) + 3O_2 \rightarrow 4(-O^- \ldots H^+) + 6H_2O + 2N_2.$$

The hydrogen zeolite can be prepared from the ammonium form also by decomposition under vacuum baking conditions[49]:

$$NH_4X = H-X + NH_3 \text{ (X is the anionic skeleton of the zeolite).}$$

Treatment of silver zeolites with aqueous solutions containing H^+ ions to replace the Ag^+ ions and anions to precipitate the silver going into solution also produces the hydrogen forms[48,50]. An aqueous solution of pyridine hydrochloride[50] can be used. In practice, H-forms are most frequently prepared from the ammonium zeolites. The hydrogen (or protonated[23]) modification has the characteristic lattice of the starting zeolite, but it has more open channels than the cationic modifications. The hydrogen form is unstable at high temperatures, and is converted into the decationated form[46] by further dehydration. Under these conditions the crystal lattice of some zeolites is disintegrated, depending on the extent of exchange. Thus, the structure of zeolite X does not break down if the exchange of Na^+ by NH_4^+ is limited[51] to 30%. With a type A zeolite, decationation is possible only up to 10%, whereas with a type Y zeolite up to 90% can be achieved[51]. Zeolites can be decationated also by electrodialysis[17]. It must be stressed that the nature of the decationated form of crystalline aluminosilicates has not been definitely established. We can only report[46] that three-coordinated aluminium atoms (Lewis-acid regions) and unpaired electron spins are present in decationated samples of zeolite Y.

III. PREPARATION OF ZEOLITE CATALYSTS

Zeolite catalysts are prepared mainly by three methods — (1) ion exchange, (2) impregnation, and (3) introduction of the catalytic component during synthesis (crystallisation) of the zeolite.

The exchange of sodium cations in prepared samples of zeolites by cations of other elements (or by H^+) and the decationation of these samples have been discussed above. These treatments yield various cationic forms (or the decationated form), possessing, as has already been said, different catalytic properties. These modifications can be treated as one of the types of zeolite catalyst.

Cation exchange can be used also to introduce metals into the zeolite structure. However, the method is restricted to elements whose cations can be reduced to the metal (by hydrogen or by alkali metals). For example, nickel-exchanged zeolite (or a zeolite containing complex cations) can be reduced by hydrogen to atomic nickel[9] at high temperature (~ 500°). In addition to nickel atoms, protons are also formed, which compensate the negative charges of the alumina–silica skeleton in place of the nickel ions:

$$[AlO_4]_2^- Ni^{2+} + H_2 \rightarrow 2Ni^0 + 2[AlO_4]^- H^+.$$

The form in which the protons exist has not been accurately established: they may enter the structure as hydroxyls. Partial decationation of the zeolite by removal of water from the hydrogen form, produced as an intermediate, is also not excluded. The result is a zeolite containing deposited metal, or, as it is called, a metal-loaded zeolite [9,52-55]. Many types of these catalysts, containing metallic phases of most of the transition elements, can be prepared. Zeolites can be loaded with metals also by adsorption of appropriate volatile or soluble compounds, organic or inorganic, of the metals on the dehydrated zeolites, followed by thermal decomposition of the compounds. The latter should decompose with deposition of the metals at temperatures below the stability threshold of the crystal lattice. The following compounds can be used — carbonyls or hydrogen carbonyls (Fe, Co, Ni, Cr, Mo, W, Mn, Re), acetylacetonates (Cr, Cu, Ag, Au), halides (Ti, Hf, Zr), alkyl derivatives, and other organometallic compounds — and the preparation and use of a number of loaded molecular sieves have been described in the patent literature [56-63]. Oxidation of the metal (e.g. Zn or Cd) in a loaded zeolite in air or oxygen produces a zeolite loaded with the metal oxide.

In some cases, introduction (or deposition) of the catalytic agent after the zeolite crystals have been prepared is unsuitable. Thus, platinum cannot be introduced by ion exchange into a CaA zeolite having 5-Å orifices, because the available platinum compounds have low pH-values and are liable to disrupt the zeolite structure, while the cations of neutral platinum ammines are larger than 5 Å. In this case the catalytically active agent is conveniently introduced at the stage of preparation (crystallisation) of the zeolite [64].

The catalytic agent can also be deposited on the zeolite particles as an external coating [65]. In multicomponent contact materials the catalytic functions of the zeolite may either combine with those of the added component or disappear. Therefore, in spite of the fact that the properties of zeolites can vary according to the conditions of application and treatment, it is probably useful to differentiate between catalysts in which the zeolites act as inert carriers for the active components and polyfunctional catalysts in which the zeolite substrate performs a specific function.

Problems of catalyst activation are closely bound up with catalyst preparation. Obviously, no single method of processing can be generally applicable to all catalysts. We can only stress the fact that removal of the water from the catalysts (albeit partial) is essential in every case, since only then are the zeolites able to adsorb molecules in their intracrystalline voids, which are the main site of reactions on zeolite catalysts. The conditions, rate, and extent of dehydration depend on the particular catalyst and on the particular process.

IV. APPLICATIONS OF ZEOLITE CATALYSTS

The first reports of the use of synthetic zeolites as catalysts were published [46,66,67] in 1960. In the following years the properties of contact materials based on various cationic forms of zeolites (types A, X, Y, mordenite, etc.) were investigated in a number of reactions, the catalysts being used both individually and in admixture, and also with additions of catalytically active metals and their compounds. These reactions, and the specific features of the zeolite catalysts, will be discussed in the following subsections.

1. Catalytic Properties of Purely Synthetic Zeolites

Weisz and Frilette [67] discovered that NaX and CaX zeolites are more active towards the cracking of n-decane at 470° than are the standard alumina–silica catalysts containing 10% of Al_2O_3. The calcium form of the zeolite was more active than the sodium form, and gave products similar to those obtained in the presence of the alumina–silica catalyst. In contrast, the products obtained on NaX contained no iso-compounds, but double the quantity of alkenes instead. Furthermore, NaX was inactive towards the dealkylation of cumene even at 510°, whereas CaX was a powerful catalyst for this reaction even at 465°. The latter material also brought about the conversion of α-pinene into camphene, but this did not occur on NaX. To account for these results, the authors suggested [68] that the reactions proceed by different mechanisms on these catalysts — by a radical mechanism on NaX, and by a carbonium ion mechanism in the presence of CaX.

The influence of the degree of exchange of Na^+ by Ca^{2+} in a type X zeolite on the catalytic activity towards the cracking of n-decane has been investigated [69]. It was shown that the activity increases with decrease in the Na_2O content of the zeolite, but it was pointed out that the deactivating effect of sodium is less marked in zeolite catalysts than in the alumina–silica catalyst.

The CaX zeolite is much less active [70] towards the cracking of cumene than is an alumina–silica catalyst of the Houdry type, but the course of the reaction is the same. Cumene was found to be adsorbed approximately twice as strongly as benzene on the CaX zeolite, whereas on alumina–silica catalysts the adsorption coefficients are nearly the same [70].

The cracking of cumene has been used as a model reaction in many studies of the catalytic activity of synthetic zeolites [31,51,71-76].

Tsitsishvili and his coworkers [71] investigated the activity of NaX, CaX, and HX zeolites, and concluded that the reaction on these catalysts was sterically hindered.

Topchieva and her coworkers [72-74] studied the catalytic activity of synthetic X and Y zeolites, and found that NaX had negligible activity: replacement of Na^+ ions by Ca^{2+} increases the activity in proportion to the extent of exchange. There was also an appreciable increase in activity on increasing the SiO_2/Al_2O_3 ratio in the zeolite. The highest rate constant was obtained with decationated samples of the Y zeolite. The authors did not observe significant adsorption of propene on the zeolites, which suggests that propene cannot inhibit the cracking of cumene on these catalysts, whereas it is known to inhibit the reaction on amorphous alumina–silica catalysts. Hence, they concluded [72,74] that the kinetic mechanism of cumene cracking is probably different on the two types of catalyst.

The adsorption of quinoline on zeolites was examined [73] in order to throw light on the nature of the active centres. With decationated samples of zeolite Y the activity initially decreased in proportion to the amount of quinoline adsorbed, and remained constant thereafter. This trend in the activity of decationated zeolites led the authors to postulate the existence of at least two types of active centre on the surface — aprotic centres, associated with aluminium atoms in the tervalent state, and AlO_4 tetrahedra.

Schwab and Sieb [75] showed that the activation energy for cumene cracking of the cationic forms of zeolite X examined

(Mg^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}) passes through a minimum as Na^+ is gradually replaced by the bivalent cation (with the exception of Cd^{2+}, with which the activation energy increases continuously). The authors' explanation is that at high degrees of exchange the replacement occurs in deep layers of the zeolite, which are not accessible to the cumene. These results are somewhat unexpected: after a certain amount of exchange, one would have expected the activation energy to remain constant.

Among the univalent cationic modifications of zeolite X (the Li, Na, K, and Rb forms), the lithium form is the most active towards cumene cracking[76] at 500°, and is comparable to an industrial alumina–silica catalyst. The authors[76] point out the proportionality between catalytic activity and the force field of the cation, and suggest that the cations act as active centres in the zeolites.

Rabo and his coworkers[31] report that the activity of Y zeolites (SiO_2/Al_2O_3 = 5) in the cracking of cumene increases in the sequence NaY < BaY < SrY < CaY ≃ MgY ≃ ≃ BeY, i.e. in the opposite order to the radii of the corresponding cations. Thus, a direct link exists between catalytic activity and the polarising power of the cations, which increases with decrease in their radius.

The activity of the centres in decationated type Y zeolites varies[51], being highest in the samples containing the greatest number of decationated regions. The authors account for the non-equivalence of the centres by three factors — (1) the presence in the zeolites of three types of crystallographically different sites for the Na^+ ions, and probably also for the decationated sites, (2) interaction between the centres, determined by the proximity of the sites, and (3) the presence of three-coordinated unsaturated aluminium centres, in addition to AlO_4^- tetrahedra, in decationated zeolites. The same workers have shown[77] that irradiation of decationated zeolites lowers the activation energy for the cracking of cumene.

The hydrogen form of synthetic mordenite has a high catalytic activity for hydrocarbon cracking[78–81]. The fission capabilities of this catalyst in the cracking of n-decane[78] are similar to those of CaX zeolite[67]. Synthetic mordenite in the H-form cracks gas oil, n-heptane, 2,4-dimethylpentane, and methylcyclohexane faster than does the commercial alumina–silica catalyst[81], giving a higher proportion of light and branched hydrocarbons among the products. Natural mordenite, previously treated with acid and converted into the hydrogen form, becomes active in cracking, alkylation, and isomerisation reactions at relatively low temperatures[82,83]. For example, the cracking of n-hexane occurs at a temperature as low as 200° with formation of saturated compounds, and benzene is converted into toluene and ethylbenzene[83] at 400°. Butane and cyclohexane rapidly isomerise to isobutane and methylcyclopentane respectively at ~ 200°, and the authors stress the fact that under these conditions deactivation of the catalyst is very slow. Thus, at 260° and under atmospheric pressure, cyclohexane (in a stream of helium) is 11.5% converted into the isomer and 0.9% into side-products. None of these reactions occurs on amorphous alumina–silica catalysts under the stated conditions. The authors conclude that acid mordenite is more closely similar to $AlCl_3$ promoted with HCl than to an amorphous alumina–silica catalyst[83].

Some interesting features of the cracking of alkanes on synthetic zeolites have been observed[84–88]. In the presence of CaA zeolite, n-dodecane decomposed without formation of cyclic compounds, which did, however, form on NaX and CaX. The reaction products obtained in the presence of CaA also contained very small amounts of branched hydrocarbons[84]. Both dehydrocyclisation and isomerisation reactions take place in the voids of the CaA molecular sieve, but because of the small size of the orifices the resulting hydrocarbons cannot escape from the voids and undergo further transformations[85,86].

Many workers have demonstrated the high activity towards hydrocarbon cracking of the rare-earth cationic forms of zeolites X and Y and of mixed metal–acid crystalline aluminosilicates[89–96]. These catalysts, in which some of the Na^+ ions have been replaced by H^+ and some by multivalent cations (Ca^{2+}, Mn^{2+}, rare-earth elements, etc.), show enhanced activity, high selectivity, and good stability[89]; they are used in the preparation of the new industrial cracking catalyst[11,89] Durabead 5.

As was mentioned above, zeolites can also catalyse many reactions besides cracking. Their polymerisation properties were the first to be observed, because these became apparent (as "parasitic" catalytic activity) when the zeolites were used for drying alkenes. Molecular sieves can be arranged in the following sequence of catalytic activity for the polymerisation of propene[97–99]: CaX > > NaX > CaA > NaA > KA = 0. The reactivity of alkenes increases iin the sequence $CH_2{:}CH_2 < CH_3.CH{:}CH_2 <$ $< (CH_3)_2C{:}CH_2$, which is consistent with the reactivities of alkenes towards an acidic catalyst in ionic polymerisation. The composition of the polymerisation products (e.g. of propene) is also similar to the composition of the products obtained when phosphoric acid on kieselguhr is used as the catalyst. Norton[97–99] suggests that the action of zeolites in the polymerisation process is bound up with the presence of acidic regions in these materials.

The polymerisation of gaseous and liquid (low-boiling) C_2–C_6 monoalkenes on crystalline alumina–silica catalysts has been proposed[100] as a method for the production of high-octane fuels for reciprocating internal-combustion engines. In the presence of CaA zeolite, isobutene polymerises even at room temperature and atmospheric pressure to give a product containing 90 vol.% of the trimer and 10 vol.% of the dimer[101].

Crystalline aluminosilicates can also catalyse isomerisation of the double bond in alkenes[102–104]. Thus, but-1-ene on CaA zeolite, at atmospheric pressure and a temperature of 80°, undergoes 71% conversion into but-2-ene, and at 220° the yield of but-2-ene reaches 85%; 2-methylbut-1-ene is 88% converted into 2-methylbut-2-ene at 100°.[103] The activity of zeolites towards the isomerisation of alkenes is increased by γ-irradiation[77,102]. The high (up to 73%) and stable (unaffected by operation for 24 h) catalytic activity of CaA zeolite in the isomerisation of 2-methylpent-1-ene is particularly interesting[104].

Alkanes and cyclic hydrocarbons also can be isomerised on synthetic zeolites. Thus, NaX catalyses[105] the conversion of cyclopropane into propene. Cyclohexane is converted into methylcyclopentane on CaX zeolite, the yield being increased by recycling[106]. Zeolites of types X and Y in their bivalent cationic forms promote the isomerisation of n-alkanes[31].

Synthetic zeolites catalyse also the conversion of alcohols. Depending on the nature of the catalyst and on the experimental conditions, alcohols are converted into ethers[107–110] or alkenes[76,78,83,90,97,107,109,111–115], or alternatively they undergo mainly dehydrogenation with formation of carbonyl compounds[16,57]. Ethers are obtained when

the zeolite used has fairly large pores, at low temperatures, and with relatively high flow rates. Dehydrogenation of alcohols was observed on type A zeolites containing chromium introduced by isomorphous substitution[16]. In every other case the alcohols suffered dehydration with the formation of alkenes. The process is sometimes complicated by side reactions, such as polymerisation and isomerisation of the double bond and of the skeleton of the resulting alkenes, hydrogenation with formation of alkanes, etc. For the dehydration of propan-2-ol[71], the zeolites can be arranged in the series HX > NaX > CaA. The reaction took place[71] at temperatures below 250° on the NaX sample, even though Frilette and Munns[114] were unable to observe any reaction even at 300°. This discrepancy may have been caused by the use[71] of a contaminated or partly hydrolysed zeolite. However, it has been reported that the NaX zeolite dehydrates alcohol in the presence of carbon dioxide. The active centres are said[114] to result from the chemisorption of CO_2 on the zeolite. A similar promoting effect of carbon dioxide on zeolite catalysts has been observed also in the cracking of alkanes, alkenes, aromatic and naphthenic hydrocarbons, and their mixtures, in the isomerisation and polymerisation of alkenes, in the polymerisation of terpenes, and in a number of other reactions[110].

The dehydration of various alcohols on NaX and CaX zeolites has been investigated[111,112]. On NaX the chain length and the amount of chain branching do not affect the degree of conversion of the alcohols: pentanol, 3-methylbutan-1-ol, and nonanol are dehydrated to the extent of 53–56% at 275° and a space velocity of 4 h^{-1}. On CaX the conversion of pentan-1-ol was significantly higher than on NaX, but the products contained a large proportion of saturated hydrocarbons (mainly isopentane), increasing rapidly with temperature, whilst the yield of pentenes decreased. Furthermore, isomerisation of the skeleton and cracking were much more extensive on this catalyst than on NaX.

The CaY zeolite (SiO_2/Al_2O_3 = 3.4) has a high activity towards the dehydration of C_2–C_4 aliphatic alcohols and cyclohexanol[109]. All the normal primary alcohols were completely converted into the corresponding alkenes on this catalyst at 250°. Cyclohexanol was dehydrated smoothly and selectively: 68% of cyclohexene was obtained even at 150°, and at 170° the reaction was quantitative. With n-butanol and isobutanol, the resulting alkenes underwent extensive polymerisation under the experimental conditions[109].

The zeolites CaX and CaY showed remarkable behaviour in the dehydration of t-butyl alcohol[115]. The fully anhydrous zeolites had very low activity, which increased, however, as the water content of the catalyst was increased. The highest activity was observed with samples containing one water molecule per cation in the unit cell. Promotion by water was reported also in the cracking of n-hexane on the rare-earth cationic form of type Y zeolite[116]. These observations should help to elucidate the mechanism by which zeolite catalysts operate.

According to the patent literature[117], molecular sieves show high selectivity and thermal stability as catalysts for the hydration of ethylene oxide to ethylene glycol.

Several papers have been published on the use of synthetic zeolites as alkylation catalysts. A patent suggests various cationic forms of the X zeolite for the alkylation of aromatic hydrocarbons by alkenes[118]. There is evidence[8] that, unlike the conventional acidic alkylation catalysts, which rapidly lose their activity in the presence of sulphur and oxygen compounds, zeolites show a high activity in the presence of these impurities even without added metallic cocatalysts. It is pointed out that thiophens and phenols can be alkylated rapidly and with good selectivity on these catalysts[7,8]. Minachev and his coworkers[119–127] studied the reactions of aromatic hydrocarbons with alkenes and alcohols in the presence of X and Y zeolites of different compositions produced in the Soviet Union and also in the presence of synthetic mordenite. They found[120,121] that the activity of zeolites of similar structure (X and Y) in the alkylation of benzene by propene at atmospheric pressure increases with increase in the SiO_2 content. They also suggested[120] that, as in the case of amorphous alumina–silica catalysts, an optimum Al_2O_3 content should exist in zeolites. A comparative study of the behaviour of the calcium forms of Y zeolite obtained from NaY by exchange with calcium chloride, nitrate, and acetate led the authors to conclude[121] that the nature of the anion of the salt has practically no effect on the activity of the catalyst. It is the cation which plays the key role in determining the catalytic activity of zeolites[121,125,127].

It is evident from Table 3 that NaY zeolite has negligible activity towards alkylation under the stated conditions: only by raising the temperature to 400° and by decreasing the flow rate of the reaction mixture to one-third of its value could the yield of cumene be raised[121] to 10%. Bivalent and tervalent cationic forms are very active, the activity of these zeolites varying monotonically with the polarising effect of the cation: the greater the charge on the cation and the smaller its radius, the higher is the polarising effect of the cation and the more active is the catalyst. The bivalent modifications with comparable degrees of cation exchange can be arranged in the series BaY < SrY < CaY ≃ CdY ≃ MgY. The tervalent cationic forms are more active (on the basis of a single cation in the unit cell) than samples with bivalent cations, but they are less stable[125]. The activities of the pure crystalline aluminosilicates of the rare-earth elements with similar degrees of exchange are practically identical (Table 3).

TABLE 3. Alkylation of benzene by propene* at 250° on various cationic forms of Y zeolite[121,127] having SiO_2/Al_2O_3 = = 4.2, with feed rate of mixture 10.2 moles $litre^{-1}$ h^{-1} (0.6 h^{-1} with respect to C_6H_6) and C_6H_6/C_3H_6 = 2.5 : 1 (molar).

Zeolite	Degree of exchange of Na^+ by M^{n+}, equiv. %	Radius of cation, Å	Yield of monopropylbenzenes, % (based on propene)	Zeolite	Degree of exchange of Na^+ by M^{n+}, equiv. %	Radius of cation, Å	Yield of monopropylbenzenes, % (based on propene)
NaY	—	0.98	trace	LaY	60	1.22	35.2
DY **	75	—	54.2	Ce^{3+}Y	61	1.18	53.1
MgY	80	0.78	37.6	Pr^{3+}Y	60	1.16	51.0
CaY	75	1.06	32.8	Nd^{3+}Y	63	1.15	51.0
SrY	80	1.27	10.6	SmY	60	1.13	52.5
CdY	76	1.03	35.4	mixed REE–Y****	15 wt. % of oxides	—	45.3
BaY	62	1.43	1.4	alumina–silica	—	—	13.7
AlY ***	57	0.57	45.5				

* Propane–propene fraction containing 75 vol. % of propene.
** Decationated form.
*** At 300°.
**** REE = rare-earth element.

Thus there is no need to use pure compounds for the preparation of rare-earth catalysts: a contact material having approximately the same activity and selectivity can be prepared from a mixture of salts of composition similar to that of the technical mixtures of rare-earth metal chlorides [127], which makes these catalysts much more readily available. The highest yield of monopropylbenzenes (containing 93–98% of cumene) is obtained with the decationated zeolite DY. An industrial amorphous alumina–silica cracking catalyst is less effective by factors of 1.5–3.5 than zeolites with sufficiently wide orifices leading to crystal voids [120,121].

The extent of exchange of sodium ions by multivalent cations also has a marked influence on the activity and selectivity of zeolite catalysts towards alkylation [121,125,127]. The yields of monopropylbenzenes and all other alkylbenzenes increase as the proportion of Na^+ ions exchanged is increased, but not uniformly: this suggests that the cation sites in the zeolite are not equivalent. Thus, in the case of calcium [121,125], samples with degrees of exchange up to 40–45% have a low activity (Fig. 1); at around 50% exchange we observe a sharp discontinuity in the increase in activity, and the conversion of propene approaches 100%: with further replacement of Na^+ by Ca^{2+} the yields of cumene and alkylbenzenes increase much more slowly, and the yield of polyisopropylbenzenes drops as a result of the change in the selectivity of the catalyst. A similar state of affairs has been reported [127] for Nd^{3+} cations, the only difference being that the neodymium zeolites exhibited considerable activity at 20–30% lower degrees of exchange of the Na^+ ions than in the corresponding calcium zeolites. This is probably due to the higher affinity of the Nd^{3+} cations (as compared with the Ca^{2+} ions) for the catalytically active regions of the zeolite, and to the greater polarising effect of the tervalent cations [127]. The use of zeolites with a high degree of exchange allows the reactions to proceed under milder conditions, and leads to improved catalyst stability. Thus, the temperature had to be raised by 150 deg to obtain the same yield from an NdY zeolite of 21% degree of exchange as from a catalyst containing three times that amount of rare-earth elements [127].

The alkylation of benzene by ethylene and by some alcohols [121,124], and of homologues of benzene by ethylene and by propene [121,124,126], has been investigated. The results

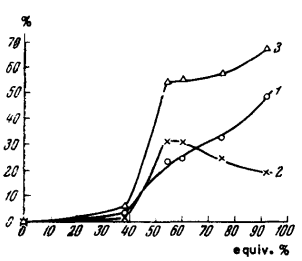

Fig. 1. Influence of the degree of exchange of Na^+ by Ca^{2+} (abscissa), at 250° with a feed rate of the mixture of 10.2 moles $litre^{-1}$ h^{-1} (0.6 h^{-1} with respect to C_6H_6) and a molar ratio of $C_6H_6 : C_3H_6$ = = 2.5, on the yield of products of the alkylation of benzene by propene (ordinate):
1) cumene; 2) polyisopropylbenzenes; 3) alkylbenzenes (monoisopropylbenzenes + polyisopropylbenzenes).

TABLE 4. Alkylation of aromatic hydrocarbons by alkenes and alcohols on CaY zeolite, having SiO_2/Al_2O_3 = 4.2 and degree of exchange > 90% at atmospheric pressure.

Aromatic hydrocarbon	Alkylating agent	Experimental conditions: temp.	feed rate of reactant mixture, moles × $litre^{-1}$ h^{-1}	A : B molar ratio	Products	Yield, %
Benzene	ethylene	400°	5.1	2	ethylbenzene diethylbenzenes	41.1 6.8
Benzene	propan-1-ol	250°	3.5	6	isopropylbenzene n-propylbenzene polyisopropylbenzenes	70.4 4.4 1.2
Benzene	ethanol	325°	3.6	6	ethylbenzene diethylbenzenes	71.5 4.7
Benzene	propan-2-ol	250°	3.5	6	isopropylbenzene n-propylbenzene polyisopropylbenzenes	72.8 2.8 2.9
Toluene	ethylene	375°	5.1	2	ethyltoluenes xylenes, ethylbenzene, polyalkylbenzenes	40.8 20.6
Toluene	propene	250°	8.7	5.3	monoisopropyltoluenes polyalkylbenzenes	74 3.7
Ethylbenzene	propene	250°	7.5	5.3	ethylmonoisopropylbenzenes polyalkylbenzenes	83.0 1.8
Isopropylbenzene	propene	250°	9.9	5.3	di-isopropylbenzenes polyisopropylbenzenes	85.1 3.2

of experiments made under the optimum conditions are given in Table 4. The yields of products are calculated on the basis of the alkenes (or alcohols) used in the reaction. In the absence of alkenes, homologues of benzene undergo disproportionation of their alkyl groups on CaY zeolite [121].

Hydrogen sulphide is oxidised to sulphur on NaX zeolite [66]. It has been found [128] to react with oxygen in the voids of zeolites, to give products which vary according to the experimental conditions and to the nature of the catalyst. Hydrogen sulphide is oxidised to sulphur trioxide at 100° on an NaA molecular sieve and at 200° on a CaX zeolite. Zeolites catalyse the vapour-phase reaction between methyl propionate and formaldehyde with formation of methyl methacrylate [129], and the condensation of organosilicon compounds [130]. Finally, it has been shown [51] that the decationated form of zeolite Y can catalyse the hydrogen–deuterium reaction. The activity of the catalysts can be increased by previous irradiation [77].

2. Zeolites as Carriers of Active Components

Under certain conditions, the zeolite substrate does not show any catalytic properties, but its adsorption properties can nevertheless have a profound effect on the activity, selectivity, and stability of catalysts. Hydrogenation is one of the most important applications of catalysts of this type. Thus, the hydrogenation of acetone to propan-2-ol has been achieved [60] on a nickel-loaded zeolite, and the selective hydrogenation of acetylene to ethylene [131] on a copper–zeolite catalyst.

Many workers [132] have examined the properties of nickel–zeolite catalysts in hydrogenations involving unsaturated hydrocarbons. A 3.8% Ni–NaA sample, prepared by cation exchange, showed high selectivity: n-octene was hydrogenated to the extent of 81.5%, whilst isoalkenes and benzene suffered practically no hydrogenation at all. The explanation is that the latter cannot penetrate to the inner voids of the zeolite, and contact the nickel. On the other

hand, a 5.8% Ni–NaA catalyst prepared by deposition effected 66.6% hydrogenation of benzene at 180°. The degree of conversion of alkylbenzenes was considerably lower (30–36%). Cyclohexene was not hydrogenated on the latter catalyst, but suffered irreversible catalytic changes (87%), whilst on a nickel-free zeolite it remained unchanged[132].

Several investigations of the hydrogenation of aromatic hydrocarbons on zeolites containing platinum-group metals have been published[7,8,63,123]. Minachev and his coworkers[123] showed that these catalysts can be arranged in the sequence

$$0.5\%\ Rh/CaY > 0.5\%\ Ir/CaY > 0.5\%\ Pd/CaY.$$

as regards their activity towards the hydrogenation of benzene. Increasing the SiO_2/Al_2O_3 ratio in the zeolite has no effect on the activity of the catalysts. Equally unimportant is the nature of the cation (Na^+ or Ca^{2+}) in the zeolite. This statement applies only up to a definite temperature, because with rise in temperature hydrogenation may be accompanied by hydroisomerisation of benzene to methylcyclopentane[123]. Under milder experimental conditions, the nature of the cation may have a significant effect[8].

As Table 5 shows, diethylbenzene is hydrogenated almost quantitatively on both palladium–zeolite catalysts at 30 atm pressure. At and below 18 atm, the sample prepared from CaY zeolite is the more active. The high selectivity and the stable activity of these catalysts are stressed[8]. Zeolite catalysts show a greater selectivity than the conventional hydrogenation contact materials towards the hydrogenation of oils of high molecular weight[133].

The unusually high stability of zeolite catalysts towards sulphur-containing catalyst poisons is of great practical importance. Thus, acetylene was almost fully hydrogenated to ethane in the presence of hydrogen sulphide, and the catalysts (containing nickel or palladium) suffered no loss of activity for several hours[8].

Hydrodesulphurisation is another reaction in which loaded zeolite catalysts are used. A hydrorefining catalyst with enhanced activity is obtained[134] by introducing cobalt as a cation into the zeolite and then impregnating the product with molybdenum oxide (MoO_3). Zeolite catalysts[8] containing small amounts of a noble metal make possible the hydrodesulphurisation of crude products having appreciably higher final boiling points than with conventional hydrofining catalysts.

Metal–zeolite catalysts have been studied also in the hydrodealkylation of alkylbenzenes[135–137]. Thus, 51.8 mole% of benzene was obtained[135] at 550° from a mixture of toluene and hydrogen (molar ratio H_2 : CH = 20) in the presence of zeolite Y containing 0.5 wt.% of platinum. The ease with which methyl groups can be removed is stated[137] to decrease in the sequence cumene > ethylbenzene > toluene, whilst the extent of hydrogenolysis of the aromatic ring increases in the same order. Addition of 0.5% of sodium to an Ni–CaA catalyst lowered the extent of hydrogenation and hydrogenolysis of the aromatic ring, and left its activity towards hydrodealkylation unaffected in the case of toluene but lowered it in the case of cumene and ethylbenzene.

TABLE 5. Hydrogenation of aromatic hydrocarbons on metal–zeolite catalysts[8].

Hydrocarbon	Diethylbenzene						Benzene
Catalyst	0.5% Pd/NaY			0.5% Pd/CaY			0.5% Rh/NaX
Temperature, °C	215	215	215	215	215	215	210
Space velocity, h^{-1}	1.5	1.5	1.5	1.5	1.5	1.5	2.0
Molar ratio H_2/CH	16	16	16	16	16	16	5
Pressure, atm	30	18	7	30	18	3.5	0 (1 atma)
Conversion, %	99	88	40	99	99	60	10

Several workers have examined the possibility of using zeolites as dehydrogenation catalysts for n-alkanes[59,84,85,87,88]. Zeolite X containing 1.95 wt.% of chromium is recommended[59] as a catalyst for the dehydrogenation of propane. Galich et al. studied the activity of catalysts, prepared from zeolites A and X, towards the dehydrogenation of n-hexane[85,87,77] and n-heptane[87], and found that the activity for these particular reactions was low[88]. The unmodified zeolites caused mainly cracking of the initial hydrocarbons, but catalysts containing Cr_2O_3 were selective for dehydrogenation. The selectivity of the contact materials was improved by adding iron and chromium oxides to the zeolites, and also by replacing sodium and calcium by nickel, cobalt, zinc, chromium, and copper cations, and by protons. The catalysts prepared from type A zeolites, which hinder the passage of aromatic hydrocarbons and isoalkanes into the product phase, were more selective than those prepared from type X zeolites. In every case the catalytic activity depended on the adsorption properties of the zeolites and of their modifications, irrespective of the method of preparation[88].

Zeolites can also be used as the basis of oxidation catalysts: thus, crystalline aluminosilicates loaded with copper, silver, or gold catalyse the oxidation of ethylene to ethylene oxide[56], and a zeolite containing TiO_2 catalyses the vapour-phase oxidation of anthracene to anthraquinone[58]. A zinc-loaded zeolite has been proposed as a catalyst for the synthesis of methanol[52], and zeolites containing metals of the iron subgroup (Fe, Co, Ni) have been proposed as contact materials for the synthesis of ammonia, the Fischer–Tropsch synthesis, and other processes[60]. Cadmium oxide on a zeolite promotes the dehydrogenation of alcohols[57].

3. Multifunctional Multicomponent Zeolite Catalysts

These are, perhaps, the catalysts of greatest practical importance, for they are used in the isomerisation of n-alkanes, hydrocracking, reforming, and various other processes, which account for the bulk of the high-tonnage production in the catalytic processing of petroleum hydrocarbons.

The high activity of zeolite catalysts in the isomerisation of n-pentane and n-hexane was recognised[46] in 1960. The zeolites examined included those of types X (SiO_2/Al_2O_3 = = 2.5) and type Y (SiO_2/Al_2O_3 = 5) in various cationic forms, containing 0.5 wt.% of platinum or palladium, and it was found that samples containing univalent cations are practically inactive. Catalysts based on the decationated and on the multivalent cationic forms of type Y zeolite were extremely active. They gave not only isomers containing a tertiary carbon atom, but also quite large amounts (11–15%) of 2,2-dimethylbutane. However, catalysts prepared from zeolites containing cations of valency 3 or higher were less selective than those with bivalent cations, and in some cases the activity fell off rapidly. Catalysts based on NaX and CaX zeolites showed practically no isomerisation activity, while decationated amorphous alumina–silica had a lower activity than DY and CaY. Studies of the effect of ion exchange showed that increasing the degree of exchange enhances the activity of the samples and allows the

reactions to proceed at lower temperatures[46]. The new isomerisation catalyst MB-5390 for the conversion of n-pentane, n-hexane, and their mixtures was developed from this work: it combines the advantages of the high-temperature (370–455°) catalysts, which give a high yield of isomers, with those of catalysts working at low temperatures (23–205°), which offer a longer useful life[12]. The activity of this catalyst did not fall off after 2000 h operation. Furthermore, the catalyst was insensitive to water and sulphur (at concentrations < 0.001%). It was subsequently shown[138] that a catalyst more resistant to sulphur is obtained if platinum is introduced into CaY zeolite by ion exchange rather than by the normal impregnation method.

Minachev and his coworkers[62,122,123,139-141] examined the properties of X and Y zeolites produced in the Soviet Union, of varying SiO_2/Al_2O_3 ratios, and containing metals of Group VIII of the Periodic Table (Pt, Pd, Ir, Rh, Ni). Some of their results are presented in Table 6. The sodium forms of the zeolites gave inactive catalysts, whereas the calcium and the decationated forms gave highly active catalysts. Contact materials based on zeolites having $SiO_2/Al_2O_3 = 4.2$ were more active than materials in which this ratio was 2.5 or 3.4.[123,141] By increasing the ratio of silica to alumina in the zeolite it was possible to raise considerably the yield of isomeric hexanes (including 2,2-dimethylbutane), and to lower the reaction temperature. The platinum and the palladium catalysts (0.5 wt.%) had similar activities, but on the rhodium and iridium catalysts hydrocracking of the initial hydrocarbons took place in addition to isomerisation of n-alkanes. Thus, on a 0.5% Rh/CaY catalyst ($SiO_2/Al_2O_3 = 3.4$) at 390° and 30 atm, with a space velocity of 1 h^{-1} and a molar ratio of $H_2/n\text{-}C_6H_{14}$ = = 3.2, the quantities of isomeric hexanes and hydrocracking products were 25.8% and 21.9% respectively, whereas on the analogous iridium catalyst at 310° they became[123,139,141] 6.3% and 26.2%. Varying the concentration of palladium in the zeolite from 0.25 to 1 wt.% had little effect on the activity of the catalyst.

The isomerisation of cyclohexane followed the same pattern as the transformations of n-alkanes[141].

TABLE 6. Isomerisation and hydroisomerisation of hydrocarbons on zeolites containing Group VIII metals[141] (30 atm; space velocity 1 h^{-1}, molar ratio $H_2/CH = 3.2$).

Catalyst	SiO_2/Al_2O_3	t, °C	Yield of isomers, wt.%	Hydrocracking products, wt.%
		n-Butane		
0.5% Pt/CaY	4.1	400	27.0	3.2
		n-Pentane		
0.5% Pd/CaY	4.1	360	50.9	3.8
		n-Hexane		
0.5% Pd/NaY	4.5	350	trace	—
0.5 Pd/CaY	3.4	400	58.0	3.2
0.5 Pd/CaY	4.5	350	70.3	3.6
0.5 Pt/CaY	3.4	400	59.4	3.8
0.5 Rh/CaY	3.4	390	25,8	21.9
0.5 Ir/CaY	3,4	310	6.3	26 2
		n-Heptane		
0,5 Pd/CaY	3.4	360	47 2	10 3
		Cyclohexane		
0.5 Pd/CaY	4.5	330	57.0	3.7
0.5 Ir/CaY	3.4	330	4.0	52.0
		Benzene*		
0.5 Pd/CaY	4.5	320	67.3	4.3
0.5 Ir/CaY	3.4	320	5.8	60,0
0.5 Rh/CaY	3.4	320	12.0	16.9

* Space velocity = 0.5 h^{-1}, $H_2/C_6H_6 = 5$.

The hydroisomerisation of benzene gave higher yields (up to 67.3%) of methylcyclopentane than could be obtained by the conversion of cyclohexane. In addition to benzene and the isomeric cycloalkanes cyclohexane was also present among the reaction products. The rhodium and particularly the iridium catalysts again showed a high activity towards hydrocracking: at 320° the former gave 16.9% and the latter ~ 60% of hydrocracking products, whilst hydroisomerisation occurred only to the extent of 12% and 5.8% respectively.

A comparison of zeolitic and conventional bifunctional isomerisation (hydroisomerisation) catalysts showed that the former are in many cases more active than the latter[141]. A given degree of conversion of hydrocarbons can be achieved on zeolite catalysts at temperatures 50–100 deg lower than on other bifunctional catalysts. Moreover, the former offer good selectivity and high stability[141]. Lastly, a metal–zeolite catalyst does not require promoters such as HCl or HF, which are normally introduced into the Al_2O_3 or added to the crude material. All these observations confirm that zeolite catalysts are superior to those currently used in industry for isomerisation reactions.

Some metal–zeolite catalysts, such as the rhodium and the iridium zeolites, show a high activity towards the hydrocracking of hydrocarbons under certain conditions[141]. These properties are found also in catalysts prepared from the rare-earth cationic forms of zeolites and the oxides or sulphides of metals in Groups VI and VIII of the Periodic Table[142,143]. Hydrocracking of high-boiling hydrocarbons can be realised also on zeolites containing metals of Group VIII.[144,145].

Zeolite reforming catalysts also have valuable properties[7,8,146,147]. Unlike platinum reforming catalysts, they are relatively insensitive to the presence of nitrogen bases in the crude material. Thus, they are unaffected for 150 h by up to 200 p.p.m. of nitrogen (in the form of quinoline) in the fraction undergoing reforming[8].

V. SELECTIVITY OF ZEOLITE CATALYSTS

Data on the use of zeolite catalysts show that the main factors determining their activity are the nature and the degree of exchange of the cation in the zeolite, the structure of the zeolite lattice, the value of the SiO_2/Al_2O_3 ratio, and the sizes of the reactant and product molecules relative to the orifices in the zeolite. Allowance for these factors enables us to make a rational choice of zeolite catalysts having the properties required for specific reactions. Other conditions being the same, the relationship between the size of the molecules and the size of the orifices leading to voids in the zeolite is particularly important. Thus[64], n-hexane (critical diameter 4.9 Å) and 3-methylpentane (5.9 Å) are not cracked on zeolite NaA, in which the orifice size is 4 Å. On CaA zeolite (5 Å), only n-hexane is converted, while 3-methylpentane cannot gain access to the voids in the zeolite and does not react under the same conditions. When a mixture of n-hexane, 2-methylpentane, and 3-methylpentane is cracked on CaA zeolite, only the straight-chain hydrocarbon is converted. It is evident from these results that zeolites show high selectivity in respect of the size and shape of molecules, and that the active centres in zeolite catalysts are mostly located within the crystal voids. The term "intracrystalline catalysis"[64,67,68,78] originated from this effect. The intracrystalline nature of catalysis by zeolites is revealed

also by other examples. Thus, n-butanol is dehydrated to the same extent (~ 60%) at 260° on CaX zeolite (~ 8 Å) and on CaA zeolite[64]. But the degree of conversion of isobutanol (critical diameter > 5 Å) at the same temperature is 85% on CaX zeolite, and less than 2% on CaA. A similar state of affairs has been observed with s-butyl alcohol: this compound was 82% dehydrated on CaX at 130°, whereas no reaction occurred on CaA. However, on raising the temperature to 210° the compound was 45% dehydrated. This shows that, according to the conditions and to the reactivity of the molecules, the reaction can occur also on the outer surface of zeolites, although this surface accounts for only 3–5% of the total surface area. The same workers[64] have selectively hydrogenated propene (in an equimolecular mixture with isobutene) on a 0.31% Pt/CaA catalyst. At 343° and under atmospheric pressure the only product of the reaction was propane (yield ~ 70%), in spite of the fact that the two alkenes have identical reactivities towards hydrogenation. It should be noted that n-alkenes (propene, but-1-ene) could be hydrogenated even at 25°. Experiments with single alkenes showed that the active centres of the platinum are not accessible to the isoalkene, which explains why the latter was not hydrogenated.

A great deal of work has been done on the selectivity of zeolite catalysts[85,90,106,107,122,148–151]. The dehydration of ethanol on CaA zeolite gave mainly ethylene, whereas the chief product of the reaction on CaX under comparable conditions was ether[107]. Selective oxidation of n-alkanes mixed with isomers can be effected[148,150].

Individual molecules which penetrate into the pores of zeolite catalysts can be converted into different substances. Some of these can escape from the pores, but others remain trapped. When this happens, the reaction follows an unexpected path, leading exclusively to the formation of some definite products. Thus, it has been shown[85] that aromatic hydrocarbons are formed in the voids of CaA zeolite, but because of their size they cannot escape from the catalyst crystals and undergo further reactions to give condensation products and carbon. The nature of these products and of the carbon deposits has been investigated[86].

Some examples of the molecular-sieve selectivity of zeolite catalysts, taken from the papers by Minachev and his coworkers[121,122,141], are given in Table 7.

However, the molecular-sieve selectivity of zeolites is not always apparent. For example, the hydration of ethylene oxide (4.2 Å) an NaA zeolite (4 Å) gives ethylene glycol and polyethylene glycol[67]. In this case the pore size does not determine the selectivity, and the reaction takes place on the outer surface of the crystal (in the secondary pore structure). Moreover, the selectivity of zeolite catalysts is not determined exclusively by the relative size of the reactants and the zeolite orifices. According to Borunova and her coworkers[132], a 7.8% Ni/NaX catalyst prepared by ion exchange affords complete hydrogenation of n-octene, whilst benzene is only 5% hydrogenated, in spite of the fact that the hydrogenation of benzene is known[152] to reach 100% on catalysts comprising 4% or more of nickel deposited on carriers.

The zeolite structure can also affect in some cases the reaction mechanism. Thus the channel structure of synthetic mordenite (H form) used as a cracking catalyst is thought[81] to enable reactant molecules to contact several acidic active centres at the same time, which may explain the high isomerisation activity of this material, resulting in a high content of branched hydrocarbons in the cracking products. The long pores in mordenite also favour a more prolonged contact between the reactant and the active surface, resulting in cracking to simpler molecules than with amorphous alumina–silica catalysts.

Thus, geometric factors in catalysis on zeolites combine with the molecular-sieve properties of these materials, which often determine not only whether or not a reaction can occur, but also the nature of the reaction and the type of products formed.

VI. OPERATING MECHANISM OF ZEOLITE CATALYSTS

Crystalline zeolitic aluminosilicates are similar to amorphous aluminosilicates, and catalyse many reactions which are accelerated by the usual aluminosilicates. The activity of zeolites is often higher than that of aluminosilicates, and increases with the SiO_2/Al_2O_3 ratio in the crystal lattice, although the cation-exchange capacity decreases. In natural clays, on the other hand, we find a relation between the cation-exchange capacity and the catalytic activity in cracking reactions[153].

TABLE 7. Selectivity of zeolite catalysts.

Catalyst	Diameter of orifices in zeolite, Å	Reaction	Conditions: temp.	Conditions: pressure, atm	Conditions: space velocity, h^{-1}	Critical diameter of molecules, Å: reactant	Critical diameter of molecules, Å: product	Yield of products, %	
0.5% Pd/CaY	~8	isomerisation of n-hexane	350°	30	1	4.9	5.6	isohexanes	2.4 70.3
0.5% Pd/CaM	4–5								
0.5% Pd/CaY	~9	hydrogenation of benzene	130°	30	0.5	5.8	6.1	cyclohexane	80
0.5% Pd/CaM	4–5								4.2
0.5% Pd/CaY	~8	isomerisation of cyclohexane	130°	30	0.5	6.1	–	methylcyclohexane	51.1: 2.6
0.5% Pd/CaM	4–5								
CaY	~8	alkylation of benzene by propene*	250°	1	0.6	5.8	–	cumene + polyisopropylbenzenes	48.2+19.1 1.3 33.1+21.1
CaM	4–5								
HM	6.6								
CaY**	~8	dehydration of cyclohexanol	170°	1	3.87	~6	5.8	cyclohexene	100
CaM	4–5								3
HM	6.6								100
CaY	~8	dehydration of ethanol	250°	1	3.87	4.7	4.4	ethylene	100
CaM	4–5								16
HM	6.6								100

* Molar ratio $C_6H_6/C_3H_6 = 2.5$.

** The SiO_2/Al_2O_3 ratio in this zeolite was 3.4; in the other cases the ratio was 4.5.

The hydrogen (and decationated) form of a molecular sieve behaves as a solid polymeric acid, and accelerates reactions to which a carbonium-ion mechanism can be assigned. The cationic forms of zeolites, on the other hand, show a different behaviour. Thus, CaX is similar to alumina–silica catalysts in its ability to dealkylate cumene, in its preferential cracking of alkenes as compared with alkanes, and in its tendency to give large amounts of branched hydrocarbons. In contrast, NaX gives cracking products similar to those obtained on pure silica or by thermal cracking. Evidently, the replacement of Na^+ by Ca^{2+} ions in a zeolite of a given structure (X) and of constant SiO_2/Al_2O_3 ratio brings about a marked change in the properties of the catalyst. It is thought that the reaction follows a radical mechanism on NaX and a carbonium-ion mechanism on CaX.[68] Another experimental fact is the uneven change in activity of the catalysts on increasing the degree of exchange of Na^+ in the zeolite by multivalent cations[61,46,121,125,127]. A promoting effect of water and of carbon dioxide on zeolite catalysts has been reported[110,114-116], and also the high stability of these catalysts towards impurity poisons in the crude materials[8,89].

One of the earliest hypotheses aimed at describing the mechanism by which zeolite catalysts operate was put forward by Rabo and his coworkers[46], who suggested that the active centres in zeolites are negatively charged AlO_4 tetrahedra. Their conclusion followed from the fact that catalysts based on the decationated form and on the bivalent cationic forms of Y zeolites have identical activities, whereas catalysts based on X zeolites have low activities. On this model, the sodium form of zeolites is inactive in the isomerisation of n-alkanes because the univalent cation fully balances the charge on the AlO_4^- tetrahedron (whatever the SiO_2/Al_2O_3 ratio in the zeolite). Replacement of Na^+ by Ca^{2+} (i.e. of a univalent by a bivalent cation) in the structure of the X zeolite does not affect the activity of the catalyst because the Ca^{2+} ion is symmetrically located with respect to two neighbouring AlO_4^- tetrahedra, and their negative charges are fully compensated (since the Si/Al ratio in an X zeolite is ~ 1.2, i.e. close to unity). In Y zeolites, on the other hand, the Si/Al ratio is twice as large as in type X, and the Ca^{2+} ions are assumed to be located unsymmetrically with respect to neighbouring tetrahedra, so that the binding energy of the cation to one of the AlO_4^- tetrahedra is low. (In planar models the distance between AlO_4^- tetrahedra increases from 2.6 Å to 5.2 Å on passing from zeolite X to zeolite Y.) The result of this dislocation of the bivalent cation is that one of the AlO_4 tetrahedra carries a negative charge, which the authors identify with an active centre.

The high activity of zeolites in which Na^+ has been replaced by a cation of valency greater than two is explained in a similar way. It is assumed that the isomerisation involves a carbonium-ion mechanism, but how the negatively charged AlO_4^- tetrahedron can induce this reaction is not made clear. As regards the cations in the zeolite, Rabo et al.[46] point to the almost complete lack of catalytic activity in catalysts containing univalent cations and to the very low activity of multivalent cationic forms of zeolites in which the Si/Al ratio is low, i.e. in which the cation density is high, and conclude that these cations contribute little or nothing to the catalytic activity of zeolites. However, this statement conflicts with experimental results showing that in a number of reactions there is a significant difference in the catalytic behaviour of the various cationic forms of zeolites. Furthermore, the possibility of varying the catalytic properties of a given crystal merely by changing the cation was found to be a typical feature of zeolites which is, as Weisz pointed out[68], unique of its kind. The nature of the cation affects the stability as well as the activity of the catalysts[46]. Also, the sodium form of type X zeolites is active in cracking, alcohol dehydration, alkene polymerisation, etc., but CaX zeolite has even greater activity in these reactions. Lastly, the originators of the above hypothesis[46] did not take account of the three-dimensional structure of zeolites, but used a simplified two-dimensional model, which could not provide sufficiently accurate values of the distance between neighbouring AlO_4^- tetrahedra (and therefore also between cations).

Because of all these facts, Pickert, Rabo, and their coworkers subsequently put forward a new model[31] according to which the catalytically active sites in zeolite catalysts are cations having a low degree of coordination to the structural oxygen ions. The activities of various cationic forms of X and Y zeolites were examined in relation to the cracking and the isomerisation of n-hexane and to the cracking of cumene. It was found that the catalytic activity of the zeolite modifications obtained by ion exchange was a function of the charge, size, and environment of the cations. The parts played by the nature of the cations and by the degree of exchange were explained in terms of the lattice structure of zeolites X and Y. In the model for the structure of these zeolites shown in Fig. 2 the solid circles denote two types of cation site, identified by X-ray diffraction analysis of a single crystal of faujasite, which is similar to the synthetic zeolites X and Y.[31] The measured average population of the S_I sites is approximately unity, while that of the S_{II} sites is about one-half. Bivalent cations at sites on an internal surface of the zeolite have only threefold coordination to oxygen ions, whereas at S_I sites between oxygen rings the cations have sixfold coordination to oxygen ions. The charge of a bivalent cation at an S_I site is fully neutralised by the negative charges of the AlO_4^- tetrahedra to which the cation is bound. On the other hand, the charge of a cation at an S_{II} site is only half neutralised. Hence, the electrostatic fields surrounding bivalent cations at the two types of site are different. Calculation shows[31] that the field strength around the cations at S_{II} sites is higher than the value needed to cause considerable shifts in the bonding electrons of the adsorbed molecules. (A field in excess of 1 V $Å^{-1}$ is sufficient to induce a large electronic

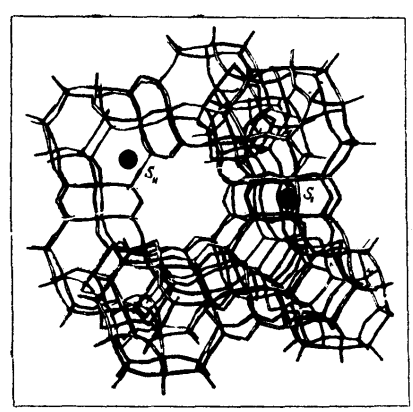

Fig. 2. Structure of the aluminosilicate framework of X and Y zeolite catalysts with two types of cation site.

shift, and in a CaY zeolite the field at these sites is greater than 6 V Å^{-1}.) It is suggested that, under the influence of the field of a cation in the zeolite, a C–H bond in an n-alkane molecule becomes polarised in the direction $C^{+}H^{-}$, which leads to the formation of a carbonium ion and to isomerisation[31]. This mechanism does not require physical removal of a hydride ion (H^{-}) with formation of an actual carbonium ion. However, the reactivity of the molecules does increase with the field strength.

The non-uniform change in the activity of a zeolite catalyst with degree of exchange of Na^{+} by bivalent (or multivalent) cations is a consequence of the non-equivalence of the cation sites. Cations at S_I sites are the first to undergo ion exchange, and most of these sites become filled with bivalent cations before the latter can begin to replace Na^{+} ions at the catalytically active S_{II} sites. In this way the authors[31] explain why a marked increase in the catalytic activity of a Y zeolite occurs only beyond about the 45–50% level of exchange. With further increase in the degree of exchange the activity of the zeolite catalyst begins to increase faster than linearly.

This model satisfactorily explains most of the experimental results. However, the difference in activity between X and Y zeolites is not convincingly explained, since according to the authors' own calculations the field strength at S_{II} sites in CaX zeolite is lower than in CaY by only 0.7 V Å^{-1}. This marginal difference can hardly account for the large difference between the two zeolites, as the authors themselves point out. They consider that, in order to resolve this inconsistency, the model must be refined, and more accurate calculations made, with fewer simplifying assumptions[31].

These views on the nature of the active centres in zeolites attracted a number of objections during the discussion at the Third International Congress on Catalysis[116]. Hirschler suggested that the activity of crystalline zeolites is due to sites akin to Brønsted acid sites, as has been postulated for amorphous alumina–silica catalysts. These sites are due to the presence in the zeolite of water, which is retained even after heating to 500° (see Table 2). This worker notes a similarity in properties between crystalline and amorphous aluminosilicates. Thus, ions of the alkali and alkaline-earth elements deactivate both the hydrogen (or decationated) form of zeolites and amorphous aluminosilicates, the poisoning effect of alkali-metal cations being considerably greater than that of alkaline-earth cations. According to Hirschler[116], the activity of both crystalline and amorphous aluminosilicates varies monotonically with their acidity.

However, important differences in behaviour between zeolites and amorphous alumina–silicas are frequently observed. For example, the hydrogen form of natural mordenite is more similar, as a catalyst, to $AlCl_3$ promoted by HCl than to an amorphous aluminosilicate[83] (see p. 907). Also, there is no direct relationship between the amount of water retained by the zeolite and the catalytic activity. Thus, MgX is less active than MgY towards the cracking of cumene and the isomerisation of alkanes, although it retains a greater proportion of water after being heated to 500° (Table 2). Hence, Rabo et al. believe[31] that the contribution of protonated sites to the carbonium-ion activity of zeolites is insignificant, for the presence of water is interpreted as a potential source of such sites.

According to Plank[116], the rare-earth cationic form of zeolite Y, when dehydrated at 650°, has very low activity towards the cracking of hexane at 204°, but treatment with water increases the activity of the catalyst many thousands of times at the same temperature. He suggests that the activity of the zeolite by water involves the reaction

$$Re^{3+} + H_2O \rightleftarrows Re(OH)^{2+} + H^{+},$$

(where Re^{3+} is a rare-earth cation), the protonated catalyst being the active form, while the salt form is inactive. The present writers[120] have expressed a similar view. The difference in stability between various catalysts based on cationic forms of zeolites X and Y has been explained[116] by the different stabilities of the zeolites HX and HY. The main function of the multivalent cations then consists in controlling the distribution and hence the stability of the acidic (H^{+}) sites: the principal difference between crystalline zeolites and amorphous aluminosilicates lies in the geometry of the acidic sites.

We must not ignore the presence of water in zeolites, since its promoting effect on zeolite catalysts is well known (in particular, towards the dehydration of t-butyl alcohol[115]). However, the "hydrolysis" mechanism described above does not appear to be generally applicable. Many experimental facts are difficult to explain from that point of view — e.g. the irregular variation in the activity of zeolites with the degree of exchange of the cations, the considerable activity of univalent cationic forms in certain reactions, etc.

Schwab and Sieb[75] have developed the so-called "two-centre" theory in order to explain the catalytic activity of zeolites. According to this theory, a reaction (such as cracking) can take place only if the catalyst contains, in addition to acidic centres, also negatively charged centres (Lewis bases). The fact that *p*-cymene is converted more readily than is cumene is claimed as evidence in favour of the hypothesis. Indeed, the presence of an electron-donor substituent (the CH_3 group) *para* to the isopropyl group causes a significant increase in the total negative charge on the nuclear carbon atom to which the isopropyl group is attached. This may result in a lowering of the activation energy for cracking, irrespective of the particular catalyst used. This theory has not been developed in detail.

Zeolites subjected to isomorphous replacement have given interesting results. Ermolenko and Pansevich-Kolyada[16] have shown that dehydration is the only reaction which ethanol undergoes on NaA zeolite. Deposition of chromic oxide (from potassium chromate) on an industrial NaA zeolite gave a catalyst which again led predominantly to dehydration. Similar behaviour was found with a sample of $Cr(OH)_3$ + NaA, prepared by mixing the zeolite with freshly prepared chromic hydroxide washed free from alkali, although this material contained 15.7% of Cr_2O_3. In contrast, a zeolite preparation in which the chromium had been introduced by isomorphous replacement caused the reaction to go mainly in the direction of dehydrogenation, with formation of acetaldehyde. The same behaviour was observed with an amorphous chromosilicate free from aluminium. However, some zeolites with isomorphous replacement, in which the SiO_2 content and the total content of Al_2O_3 and Cr_2O_3 were similar to those in NaA, proved to be catalysts of mixed type and gave approximately equal amounts of hydrogen and ethylene. These results suggest that lattice tetrahedra also can take part in some reactions. Unfortunately, the authors did not examine the behaviour of CrA zeolite prepared by ion exchange: this would have made the situation clearer.

Panchenkov and his coworkers [154] have developed some interesting ideas on the mechanism of the action of aluminosilicate catalysts. They suggest that catalysis on these materials involves reversible changes, under the influence of a reactant molecule, in the coordination of a metal ion in the crystal lattice, from a lower to a higher value. The most active centre is aluminium in fourfold coordination. The greater activity of zeolites may simply be due to the fact that the aluminium is exclusively four-coordinated, whereas in amorphous aluminosilicates the coordination number may vary (4, 5, 6, 8).

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KINETICS AND MECHANISM OF THE REACTIONS OF ISOCYANATES WITH COMPOUNDS CONTAINING "ACTIVE" HYDROGEN

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1. INTRODUCTION

Research workers and technologists have recently been showing great interest in the reactions of isocyanates with alcohols and other compounds containing "active" hydrogen. The reason is that these processes underlie the preparation of several present-day chemical products [1-3].

The reaction of the isocyanate NCO group with an alcoholic hydroxyl is an act of chain propagation in the synthesis of polyurethanes, and has therefore been studied rather more thoroughly than other reactions of isocyanates. In contrast to many known reactions involving nucleophilic addition, however, investigation of the reactions of isocyanates is only in its initial stages.

A few reviews have been published [1,4] on the reactions of isocyanates, but fresh results make it necessary to re-examine several accepted ideas. Furthermore, many aspects of the kinetics and mechanism of these reactions are not yet clear, and demand new quantitative investigations.

2. STRUCTURE OF ISOCYANATES AND SOME OF THEIR PROPERTIES

The nature of the reactions undergone by isocyanates and their mechanism are largely determined by the structure of the NCO group and the distribution of electron density in the isocyanate molecule.

The isocyanate group NCO has a linear structure [5-7]. The angle between the R–N and N–C bonds in isocyanates RNCO varies with the nature of the group R. [5-8] There is probably no appreciable conjugation between the R and NCO groups in alkyl isocyanates, as is indicated, for example, by the low energy barrier of 49 ± 3 cal mole^{-1} to rotation of the methyl group in methyl isocyanate [6]. Thermochemical calculations suggest that the conjugation energy in isocyanates is small. According to Pauling [9] it does not exceed 7 kcal mole^{-1} in methyl and ethyl isocyanates. New data on the heats of combustion of isocyanates [10] and on the mean bond energies [11] yield a conjugation energy close to zero for methyl, ethyl, and phenyl isocyanates. This is understandable when it is remembered that the N=C and C=O π-bonds in the –N=C=O group are formed by carbon by means of p_y- and p_z-electrons, and are located in perpendicular planes. Nevertheless, the N=C and C=O interatomic distances in methyl isocyanate and isocyanic acid, measured by an electron diffraction method [5], indicate that these bonds are stronger than ordinary double bonds.

Table 1 shows that isocyanates RCNO possess large dipole moments, to which a substantial contribution is made by the NCO group. The fact that the dipole moment decreases† on passing from alkyl isocyanates to HNCO, i.e. with increase in the $R(\delta^+)-N(\delta^-)$ dipole from μ_{CN} = = 0.61 D to μ_{HN} = 1.42 D, [15] indicates that the sign of the moment of the NCO group is opposite to that of the R⇌N bond. Hence the nitrogen atom in the NCO group can be assumed to be more negative than the oxygen atom. This view is supported also by the increase in dipole moment on passing from isocyanates to isothiocyanates, which can be interpreted as resulting from replacing the oxygen atom in NCO by the less electronegative sulphur (according to Pauling [9] the electronegativities of oxygen and sulphur are 1.4 and 0.4 eV respectively).

The chemical behaviour of isocyanates agrees most completely with a distribution of charge and electron density in the NCO group represented by conjugation of the valency structures (I)–(III) [6,9]

$$\underset{\text{(II)}}{R-\ddot{\overline{N}}-\overline{\ddot{C}}=\ddot{O}:} \longleftrightarrow \underset{\text{(I)}}{R-N=C=O} \longleftrightarrow \underset{\text{(III)}}{R-\ddot{N}=\overset{+}{\ddot{C}}-\ddot{\overline{O}}:}.$$

TABLE 1. Dipole moments μ of some isocyanates and isothiocyanates.

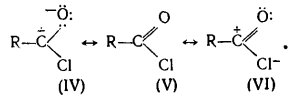
Compound	HNCO	CH_3NCO	C_2H_5NCO	C_4H_9NCO	HNCS	CH_3NCS	C_2H_5NCS	C_4H_9NCS
μ, D	1.59 [12]	2.81 [6]	2.81 [13]	2.3 [13]	1.72 [14]	3.18 [13]	3.31 [13]	3.0 [13]

† The decrease in the dipole moment of RNCO and RNCS when the alkyl radical is replaced by hydrogen is larger than would follow from vectorial addition of the dipoles [6].

TABLE 2. Rates of reaction of phenyl isocyanate with various compounds in toluene at 80° [17].

Compound	$10^4 k$, litre × mole^{-1} s^{-1}	Relative rate	Compound	$10^4 k$, litre × mole^{-1} s^{-1}	Relative rate
Butan-1-ol	30	1500	Butyric acid	2	100
Water	6	300	Butyranilide	0.3	15
Diphenylurea	2	100	Ethyl phenylcarbamate	0.02	1

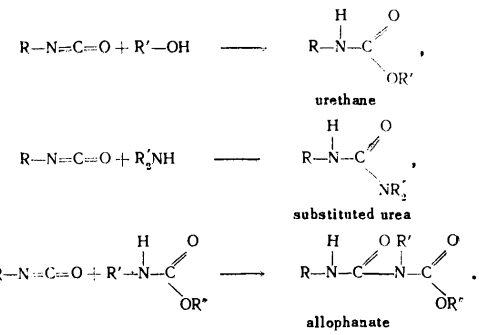
The carbon of the NCO group is a strong acceptor, resembling in several of its properties the carbon of an acid chloride — structures (IV)–(VI)



(IV) (V) (VI)

The nitrogen and the oxygen in the NCO group generally carry a negative charge, and possess electron-donor properties. This group is therefore subject to both nucleophilic and electrophilic attacks.

In most cases isocyanates behave as electrophilic reagents. Their most typical reactions are nucleophilic additions involving substances containing oxygen and nitrogen, e.g.



urethane

substituted urea

allophanate

Few thermodynamic data are available on additions to isocyanates. We can mention only the paper by Lovering and Laidler [16], who measured the heats of reaction of certain aryl isocyanates with butyl alcohols.

In the absence of catalysts, the reactivity of different nucleophilic compounds towards an isocyanate usually varies in the sequence

$$RNH_2 > ROH > H_2O > C_6H_5OH > RSH > RCOOH,$$

the sequence for amines being

$$R_2NH > RNH_2 > NH_3 > C_6H_5NH_2,$$

and that for nitrogen-containing compounds

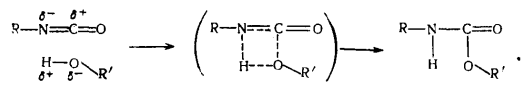
$$\underset{\text{amine}}{RNHR'} > \underset{\text{urea}}{RNHCONHR'} > \underset{\text{amide}}{RNHCOR'} > \underset{\text{urethane}}{RNHCOOR'}.$$

Numerical values of the relative rates are given in Table 2.

3. KINETICS OF THE REACTION OF ISOCYANATES WITH ALCOHOLS

The interaction of isocyanates with alcohols has been more thoroughly studied than other reactions, but even in this case the mechanism is still far from clear. Several possible reaction schemes are now being discussed in the literature, a common feature being the assumed nucleophilic attack by the alcohol or other reagent on the NCO group of the isocyanate. Non-catalytic nucleophilic addition of an alcohol to an isocyanate can be imagined as occurring in several ways. Analogous schemes may be suggested for the reactions of thiols as well as of isothiocyanates.

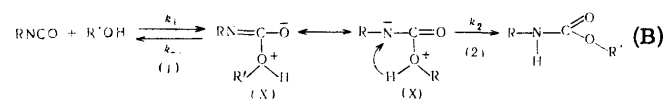
(A) Direct addition of R'OH to RNCO with the formation of a four-membered activated complex [18–20]:



(A)

Preliminary coordination corresponding to the relative arrangement of molecules in the activated complex is inherent in the formation of solvates. This mechanism is supported by the large negative entropies of activation in the non-catalytic reactions of isocyanates with alcohols [16]: in the reaction of *p*-chlorophenyl isocyanate with methanol in heptane [21], for example, $\Delta S^{\neq} = -44.5$ e.u. with $E = 8.2$ kcal mole^{-1}.

(B) Preliminary reversible addition with formation of an intermediate complex (X) of ionic structure by the scheme accepted for the reactions of other carbonyl compounds [22,23], and its subsequent unimolecular conversion into the urethane by prototropic rearrangement:



(B)

This scheme resembles that proposed by Zahradník [24] for the reactions of isothiocyanates with the hydroxide ion in aqueous–dioxan and aqueous–alcoholic solutions. The large positive values of the parameter ρ in the Hammett equation (see Section 5) observed in the reactions of isocyanates and isothiocyanates support mechanism (B) provided that (*a*) the rate of the process is limited by the nucleophilic attack (1), or (*b*) reaction (1) is rapid and reversible, the equilibrium constant increasing with increase in the electrophilic character of the substituent in group R (e.g. in phenyl).

Schemes (A) and (B) are indistinguishable by formal kinetic criteria. In both cases the reaction velocity is described by the second-order equation

$$-dC_{RNCO}/dt = kC_{RNCO}C_{R'OH}. \qquad (3)$$

For scheme (A) we have $k = k_{true}$. For scheme (B) with (*a*) $k_1 C_{R'OH} \ll k_{-1}, k_2$, we have $k = k_1 k_2/(k_{-1} + k_2)$, or in the limit, when $k_2 \gg k_1$, we find that $k = k_1$; or with (*b*) $k_1 C_{R'OH} \gg k_2$ (equilibrium), we obtain $k = Kk_2$, where K is the equilibrium constant for stage (1).

(C) Formation of the addition product X in the first stage, as in scheme (B), and its conversion into the urethane by a bimolecular reaction with a second R'OH molecule:

$$\begin{aligned} RNCO + R'OH &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X, \\ X + R'OH &\xrightarrow{k_2} RNHCOOR'. \end{aligned} \qquad (C)$$

Scheme (C) was suggested by Baker and his coworkers [25,26] to explain the increase, observed under certain conditions, in the second-order rate constant with the alcohol content of the mixture. In fact, with $k_1 C_{R'OH} \ll k_{-1}, k_2$, when the

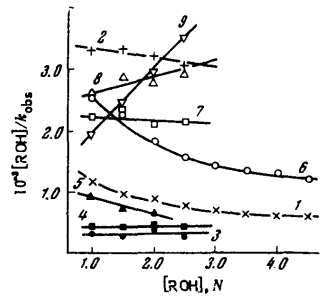


Fig. 1. Reactions of phenyl isocyanate with alcohols and glycols:
1) ethanol; 2) 2-ethoxyethanol; 3) trimethylene glycol; 4) tetramethylene glycol; 5) hexamethylene glycol; 6) ethylene glycol; 7) diethylene glycol; 8) triethylene glycol; 9) tetraethylene glycol[27].

method of quasi-stationarity with respect to the intermediate product is applicable, we have for the rate of the process, in conformity with scheme (C), the equation

$$-dC_{RNCO}/dt = \\ = k_2 C_{RNCO} C^2_{R'OH}/(k_{-1} + k_2 C_{R'OH}). \quad (4)$$

Consequently, if we start from Eqn. (3) in analysing the rate of the process, the "second-order constant" observed here will be the apparent parameter

$$k_{obs} = k_2 C_{R'OH}/(k_{-1} + k_2 C_{R'OH}). \quad (5)$$

Many facts have now been accumulated to indicate that in most cases the second-order relation is strictly satisfied up to considerable extents of conversion in reactions of both monomeric and polymeric compounds[21,27]. There are also data which in several instances do not support Baker's mechanism. Thus Robertson[28], in a kinetic study of the reaction of phenyl isocyanate with a series of alcohols and glycols, has obtained results which in most cases are not described by Eqn. (5): i.e. a linear relationship between C_{ROH}/k and C_{ROH} having a positive slope is not observed (Fig. 1).

4. EFFECT OF THE PROPERTIES OF THE MEDIUM ON THE REACTION OF ISOCYANATES WITH ALCOHOLS

The dependence of the second-order rate constant on the concentration of alcohol in certain solvents, which has been observed by several authors, is probably associated not so much with "catalysis" by the alcohol as with the change in polar and other properties of the medium. Together with Tiger[29,30] we have established, for example, that the rate constant for the reaction of phenyl isocyanate with methanol is increased by increasing the concentration of the alcohol in dioxan solution. However, a similar increase in the rate constant is observed if the concentration of the polar dichloroethane is increased while the alcohol concentration is kept constant. Since a linear relation between the logarithm of the rate constant and Kirkwood's function $(\epsilon - 1)/(2\epsilon + 1)$ (where ϵ is the dielectric constant of the medium) is maintained in both cases, it may be concluded that it is the increase in polarity of the medium produced by adding the alcohol and the dichloroethane which is responsible for the increase in the reaction rate constant. The fact that reaction velocity increases with increase in the dielectric constant of the medium is indicated also by kinetic data on the reaction of hexamethylene di-isocyanate with alcohols in the sequence of solvents[31] toluene < *o*-chlorobenzene < nitrobenzene.

Thus the conclusion reached by Ephraim et al.[32], that increase in polarity of the medium results in suppression of the reaction, is incorrect. It is probable that, apart from polarity, specific interaction between solvent molecules and the alcohol and isocyanate molecules plays an important part in the action of the solvent on the reaction velocity. Such interaction usually results in deactivation of the reactant molecules. For example, a weakly polar solvent, which undergoes no specific interaction with the reactants, is able to accelerate the reaction. Thus, according to data obtained together with Tiger[29,30], the reaction of phenyl isocyanate with methanol becomes more rapid with increasing proportion of heptane in a mixed heptane–dioxan solvent, although the dielectric constant of the system is unchanged.

5. DEPENDENCE OF RATE OF REACTION ON STRUCTURE OF ISOCYANATE

The activity of the isocyanate group is fundamentally affected by the structure of the radical R in the RNCO molecule. In conformity with the electronic structure of NCO discussed above, electron-attracting radicals will increase the fractional positive charge on the carbon, and electron-donating radicals will diminish it.

Aromatic isocyanates are usually more active than aliphatic and aralkyl isocyanates[33]. However, results obtained by different workers yield quantitative comparisons of their reactivities which show significant differences. In the case of reaction with n-butanol in the presence of triethylamine in toluene at 37°, for example, the rate constants k' and k'' (for the first and second isocyanate groups respectively in a di-isocyanate) are[34] 330×10^{-4} and 28×10^{-4} litre mole^{-1} s^{-1} for 4-methyl-1,3-phenylene di-isocyanate, while the corresponding rate constants for hexamethylene di-isocyanate are 0.83×10^{-4} and 0.42×10^{-4} litre mole^{-1} s^{-1}. In the case of reaction with a polyethylene glycol adipate at 100° we have[35] $k = 36 \times 10^{-4}$ litre mole^{-1} s^{-1} and $E = 11$ kcal mole^{-1} for the above methylphenylene di-isocyanate, compared with values of 8.3×10^{-4} litre mole^{-1} s^{-1} and 11 kcal mole^{-1} for hexamethylene di-isocyanate.

The work of Sato[27] and of Greenshields et al.[31] shows that, at high degrees of conversion, the kinetics of the reaction of alkyl or alkylene isocyanates with alcohols diverges appreciably from a bimolecular law, owing to the greater sensitivity of the rate of the process to the catalytic effect of the urethane. In the view of the latter workers[31], the kinetics of the interation of hexamethylene di-isocyanate with butan-2-ol and with polyethylene glycol in toluene are described by the equation

$$dx/dt = \alpha(a-x)(b-x)^2 + \beta(a-x)(b-x)x, \quad (6)$$

where x is the instantaneous concentration of the urethane, a and b are the initial concentrations of the isocyanate and the alcohol respectively, and α and β are constants.

In the case of aryl isocyanates the introduction of substituents into the benzene ring changes the activity of the

TABLE 3. Hammett σ-constants for NCO and other substituents.

Substituent	σ from Ref.39	σ from Ref.38	Substituent	σ from Ref.39	σ from Ref.38
p-NO_2	1.27 *	—	*p*-NHCOOR **	—	0.038
m-NCO	0.43	0.30	*p*-$(CH_3C_6H_4NHCOOC_2H_5)$	0.01	—
p-NCO	0.35	0.24	*p*-$NHCOOC_4H_9$-n	−0.05	—
p-Cl	0.23 *	—	*p*-$(CH_3C_6H_4NHCOOC_4H_9$-n)	−0.05	—
p-$(CH_2—C_6H_4—NCO)$	0.04	—	*m*-CH_3	−0.07 *	—
m-$NHCOOC_4H_9$-n	0.01—0.06	—	*p*-CH_3	−0.17 *	—
m-NHCOOR **	—	0.025			

* From Hammett's results [37].

** R = 2-ethylhexyl.

NCO group. On substitution of phenyl isocyanate the reaction velocity varies in conformity with the Hammett equation [37]

$$\log(k_{subst}/k_0) = \rho\sigma, \quad (7)$$

where k_0 and k_{subst} are the rate constants for the unsubstituted and the substituted phenyl isocyanate, σ is a parameter characteristic of the substituent, and ρ is a parameter characteristic of the type of reaction and its sensitivity to the action of the substituent. The results of different authors [38,39] indicate that ρ = 1.69–1.98. It is interesting that ρ = 1.7 for substituted isothiocyanates [40]. A positive value of ρ indicates that the reaction is accelerated by the introduction of electron-attracting substituents.

Values of σ for NCO and urethane groups, like those of ρ, have not yet been determined sufficiently accurately for calculation of the reaction velocity of individual NCO groups in substituted and multifunctional isocyanates. Table 3 gives the values of σ obtained from a comparison of the reaction velocities of isocyanates with alcohols. It includes for comparison values of σ for other substituents from Hammett's data.

No results have been published on the effect of *ortho*--substituents on the activity of aryl isocyanates. This effect can be estimated by means of the Taft equation [37]. Furthermore, values of ρ usually change with variation in the temperature and in the solvent, and without a knowledge of these it is impossible to calculate the rate constants for substituted isocyanates. Results obtained by us together with Tiger [29,30], for example, indicate that the parameter ρ = 3.3 for the uncatalysed reaction of substituted phenyl isocyanates with methanol in heptane, this value falling on addition of dioxan to the heptane, and reaching 2.6 in pure dioxan.

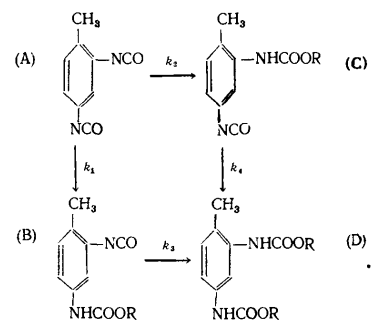
6. KINETIC FEATURES OF THE REACTION OF DI-ISOCYANATES WITH ALCOHOLS

The possibility of calculating in advance the rate constant, for interaction with an alcohol, of each of the NCO groups in a di-isocyanate is not only of theoretical but also of great practical importance. The unequal reactivities of the two NCO groups has a fundamental effect on the kinetics of the formation of the polyurethane, its average molecular weight, and the character of the molecular-weight distribution [41]. This appears especially clearly in one of the most widely used technical products — a mixture of 2- and 4-methyl-1,3-phenylene di-isocyanates.

The difference in reactivity between the NCO groups should be especially marked in 4-methyl-1,3-phenylene di--isocyanate, since the group in position 1 is not "blocked" by the methyl substituent, it is activated by the isocyanate group in position 3, and the second NCO group reacts mainly only when substitution by the urethane group has already occurred in position 1. Consequently the numerous published values for k' and k'' in di-isocyanates actually represent in the former case (k') mainly the reactivity of the first, most active NCO group in the di-isocyanate, and k'' (indirectly) the reactivity of an isocyanate group which is now present in an alkoxycarbonylaminophenyl isocyanate, not in a di-isocyanate. After reaction of the more active NCO group in position 1 in 4-methyl-1,3-phenylene di-isocyanate, for example, the NCO group in position 3 is now accompanied by a new *meta*-substituent — the urethane group — and the parameter σ changed from ~ 0.43 to close to zero. With ρ = 2, this corresponds, as follows from the Hammett equation, to an almost tenfold increase in the rate constant, which can by no means be neglected, as is done by Ferstandig and Scherrer [33].

The use above of the terms "mainly" and "indirectly" is not accidental. The point is that calculation of the rate constants from two linear sections in the anamorphoses of the kinetic curves, as is done by the authors of almost all existing papers, is sometimes not altogether correct, and frequently altogether incorrect. Let us consider this in greater detail.

If we carry out the reaction of 4-methyl-1,3-phenylene di-isocyanate with excess of an alcohol ROH, we must distinguish four pseudounimolecular reactions:



The variation in the total concentration of isocyanate groups [NCO] = 2[A] + [B] + [C] can be represented by the equation

$$[NCO] = [A]_0\left\{2e^{-(k_1+k_2)t} + \frac{k_1}{k_3-k_1-k_2}\left[e^{-(k_1+k_2)t} - e^{-k_3t}\right] + \frac{k_2}{k_4-k_1-k_2}\left[e^{-(k_1+k_2)t} - e^{-k_4t}\right]\right\}. \quad (8)$$

Brock [39] used the Hammett equation to estimate the ratios between k_1–k_4, and adopted the values $k_2 = 0.34k_1$, $k_3 = 0.0745k_1$, and $k_4 = 0.219k_1$. Putting $k_1 = 0.01$, he plotted by means of the above equation the time variation in the concentrations of the compounds A, B, and C and in the total concentration of isocyanate groups. When log [NCO] is plotted against t, an anamorphosis is actually obtained consisting of two linear sections, from which the apparent rate constants k' and k'', which do not correspond to the true values k_1 and k_2, can be found. In fact values of k' = = 0.0053 and k'' = 0.001 were obtained, instead of the values $k_1 = 0.01$ and $k_2 = 0.034$ originally introduced into the calculation.

Values of the constants and their ratios, obtained by different authors under closely similar conditions, often differ substantially from one another. Table 4 gives rate constants for reaction of the two NCO groups in 4-methyl--1,3-phenylene di-isocyanate with alcohols. The data of

TABLE 4. Rate constants for the reaction of 4-methyl-1,3-phenylene di-isocyanate with alcohols according to various workers.

Temp., °C	Solvent	Reactant	$10^4 k'$, litre mole^{-1} s^{-1}	$10^4 k''$, litre mole^{-1} s^{-1}	k'/k''	E', kcal mole^{-1}	E'', kcal mole^{-1}	Ref.
30	chlorobenzene	diethylene glycol adipate	0.45	0.057	7.9	9.3	12.6	42
25	xylene	n-butanol	0.62	0.25	10.5	8.5	10.5	42
35	xylene	n-butanol	4.22	0.44	9.6	—	—	42
25	toluene	n-butanol	13.0	0.42	31.0	1.0	—	42
21.4	toluene	n-butanol	25.5	20.5	12.4	3.1	3.6	34
40	toluene	ethanol	27.6	1.3	21.3	11.0	—	33

TABLE 5. Rate constants ($10^4 k$, litre g-equiv.$^{-1}$ s^{-1}) for the reaction of phenyl isocyanate with alcohols in toluene at 30° (catalyst concentration 10^{-4} M; [NCO] : [OH] = 1) [46].

Catalyst	$k \cdot 10^4$ л/экв·сек											
	1-C_4H_9OH	2-C_4H_9OH	$\frac{k_{prim}}{k_{sec}}$	POEG*	POPG*		methoxypropanols			k_A/k_B	k_A/k_C	k_B/k_C
					k_{prim}	k_{sec}	A = 3,1	B = 2,1	C = 1,2			
No catalyst	0.9	0.3	3.0	—	—	—	0.5	0.4	0.2	1.2	2.5	2.0
Dibutyltin(IV) dilaurate	290.0	24.2	12.0	151 **	17.5	6.6	262.0	75.7	15.2	3.5	12.2	4.9
Tin(II) octanoate	12.0	3.4	3.5	—	—	—	60.3	—	48.5	—	1.2	—
Tin(II) oleate	6.9	2.0	3.5	—	—	—	40.4	—	41.4	—	1.0	—
Lead(II) naphthanate	6.3	0.9	7.0	—	—	—	32.0	106.5	68.0	0.3	0.5	1.6

* From Ref. 47; POEG = polyoxyethylene glycol; POPG = polyoxypropylene glycol.

** Catalyst concentration 0.5 × 10^{-4} M.

Morton and Deisz [42] differ markedly from those obtained by Tazuma under similar conditions. The constants k' and k'', calculated by Burkus and Eckert [34] from a simple two-stage scheme using Frost's improved method [43] in the case of the unsymmetrical 4-methyl-1,3-phenylene di-isocyanate, are composite quantities, which do not reflect the reactivities of the two NCO groups.

With rise in temperature the difference in reactivity of the NCO groups in a di-isocyanate and the urethane–isocyanate is usually smoothed out, and the break in the anamorphosis of the kinetic curve disappears. This occurs earlier the less marked the inductive or steric interaction between the two reaction centres in the di-isocyanate. Even with 4-methyl-1,3-phenylene di-isocyanate the anamorphosis of the kinetic curve has no breaks at 100°. In the case of diphenylmethane *pp'*-di-isocyanate the anamorphosis has no break up to 70% conversion even at 30°. [1]

It is quite clear that constants for the individual stages in such multistage consecutive and parallel reactions as those of unsymmetrical di- and tri-isocyanates can be obtained only by means of electronic computers. An example is provided by the work of Ferstandig and Scherrer [33], who give a series of reliable values of the constants for several symmetrical aryl and aralkyl di-isocyanates.

7. DEPENDENCE OF RATE OF INTERACTION OF ISOCYANATES WITH ALCOHOLS ON THE STRUCTURE OF THE ALCOHOL

The activity of an alcohol depends both on the position of the hydroxyl and on the presence of substituents in the molecule. Available data are unsystematic and frequently contradictory. However, it has been firmly established that primary hydroxy-groups are more active than secondary hydroxyls. According to Lovering and Laidler [16], for example, the observed rate constants for the reactions of phenyl isocyanate with n-C_4H_9OH, iso-C_4H_9OH, and s-C_4H_9OH in alcohol at 25° are respectively 4.6 × 10^{-4}, 3.0 × 10^{-4}, and 1.44 × 10^{-4} litre mole^{-1} s^{-1}. Dyer et al.[44] obtained values of 4.4 × 10^{-4} and 1.4 × 10^{-4} litre mole^{-1} s^{-1} for the reaction rate constants of phenyl isocyanate with n-C_4H_9OH and s-C_4H_9OH in xylene at 25°.

The rate constants for the reaction of methylphenylene di-isocyanate with glycols at 40° are 0.4 × 10^{-4} and 0.78 × × 10^{-4} litre mole^{-1} s^{-1} for polyoxypropylene glycol and polyoxyethylene glycol [45].

t-Butyl alcohol reacts still more slowly. Thus according to Baker [25,26] the rate constants for the reaction of phenyl isocyanate in dibutyl ether at 20° with the series of alcohols CH_3OH, C_2H_5OH, $CH_3CH(OH)CH_3$, and t-C_4H_9OH are (0.28, 0.48, 0.23, and 0.008) × 10^{-4} litre mole^{-1} s^{-1}.

However, the difference in rates is especially large for the catalysed reactions. According to Wissman et al.[45], for example, the rate constants for the reactions of methylphenylene di-isocyanate with glycols at 40° in the presence of 0.005% of dibutyltin dilaurate are 0.87 × 10^{-4} and 27.1 × 10^{-4} litre mole^{-1} s^{-1} for polyoxypropylene glycol and polyoxyethylene glycol.

Both the absolute rates of reaction of primary and secondary alcohols with isocyanates and their ratio depend on the nature and concentration of the catalyst. Data for a series of alcohols with phenyl isocyanate in toluene solution show (Table 5) that dibutyltin dilaurate has a particularly strong effect in increasing the difference in reaction velocity between primary and secondary hydroxy-groups. It is interesting that with polyoxypropylene glycol two stages can be observed, with constants k_{prim} and k_{sec}, characterising interaction of phenyl isocyanate with the primary and the secondary hydroxyls of the diol respectively [47]. However, it is difficult to assume that the investigators were able to separate quantitatively these two stages of the reaction. Both constants are evidently effective values.

The reactivity of a molecule is diminished by the introduction of electron-attracting substituents, owing both to a decrease in the basic character of the oxygen of the hydroxy-group and to the appearance of steric hindrance. Thus the following rate constants have been determined for the reaction of 3,3-dinitropentamethylene di-isocyanate with alcohols in dimethylformamide at 30° [48]

	k, litre mole^{-1} s^{-1}
Propane-1,3-diol	3×10^{-4}
3,3-Dinitropentane-1,5-diol	0.29×10^{-4}
2,2-Dinitropropane-1,3-diol	0.064×10^{-4}

Detailed investigations of the reactions of nitro-alcohols with phenyl isocyanate have recently been made by Solodova [49] (Table 6). The change in reactivity on passing from primary to tertiary alcohols is found [49] to be less marked with nitro-alcohols (Table 7), which is attributed to steric causes. Since the nitro-alcohols already contain "bulky" nitro-groups, which cause strong steric blocking of the hydroxyls, the introduction of alkyl groups (in the case of secondary and tertiary alcohols) has less effect on the activity of the alcohol.

Introduction of a methoxy-group into an alcohol molecule enhances its activity in comparison with a methyl or an ethyl group. For the reaction of 4-methyl-1,3-phenylene di-isocyanate in ethyl acetate at 78°, for example, the rate constants with 2-methyl-2-nitropropane-1,3-diol and with 2-hydroxymethyl[methoxymethyl(?)]-2-nitropropane-1,3-diol are respectively 14.6×10^{-4} and 40.0×10^{-4} litre × × mole^{-1} s^{-1}.

The chain lengths of polymeric diols have an extremely important effect on the reactivity of their terminal groups. Although very little information has been published on this topic, the available data suggest that the degree of polymerisation has a slight effect on the rate constant [28,36,45,50] (Table 8). At low degrees of polymerisation, when the length of the glycol chain is 3–6 monomer units, some variation in the rate constant with the number of units is observed. However, the fact that the type of variation depends on the concentration of the diol (Table 9) suggests rather that the ratio between terminal groups and groups in the chain influences the properties of the medium, and hence the reaction velocity.

The degree of multifunctionality of polyols has little effect on the rate constant per equivalent (Table 10).

TABLE 6. Rate constants for the reaction of phenyl isocyanate with some nitro-alcohols in ethyl acetate at 50° ([NCO] = [OH] = 0.6) [49].

Alcohol	$10^4 k$, litre mole^{-1} s^{-1}	$k_{alc}/k_{nitroalc}$
Ethanol	34.6	17.9
Nitroethanol	1.93	—
Propan-2-ol	10.5	7.37
1-Nitropropan-2-ol	1.42	—
t-Butyl alcohol	3.9	7.2
1-Nitro-2-methylpropan-2-ol	0.54	—

TABLE 7. Relative activities of alcohols and nitro-alcohols [49].

Alcohols	Tertiary	Secondary	Primary
Simple alcohols	1	2.7	8.9
Nitro-alcohols	1	2.6	3.6

TABLE 8. Effect of chain length of polyoxypropylene glycol on its reactivity with methylphenylene di-isocyanate at 50° [45].

Equiv. wt. of polyol	Concn. of OH groups, N	$10^4 k$, litre × × g-equiv.$^{-1}$ s^{-1}
980	0.8	1.0
525	1.49	1.3
388	1.88	1.3
680	0.8	1.0
525 + toluene*	0.89	0.7
388 + toluene*	0.89	0.8

* Toluene added in these experiments to maintain the OH concentration constant with change in the molecular weight of the polyol.

TABLE 9. Dependence of rate constant ($10^4 k$, litre g-equiv.$^{-1}$ min^{-1}) on structure and concentration of diols in dioxan as solvent at 30° ([C_6H_5NCO] = 0.2 M) [28].

Glycol	[ROH], N		
	0.2	1.0	2.0
C_2H_5OH	—	7.74	20.5
$HOCH_2CH_2OH$	1.02	3.78	10.5
$HO(CH_2CH_2O)_2H$	1.56	4.32	9.18
$HO(CH_2CH_2O)_3H$	1.92	3.66	6.84
$HO(CH_2CH_2O)_4H$	2.84	4.86	6.24
$HO(CH_2)_3OH$	—	22.1	39.6
$HO(CH_2)_4OH$	—	19.2	37.9
$HO(CH_2)_5OH$	—	9.8	26.3

TABLE 10. Reaction of methylphenylene di-isocyanate with polyoxypropylene glycol (of mean equivalent weight 1000) at 60° [45].

Alcohol*	$10^4 k$, litre × × g-equiv.$^{-1}$ s^{-1}	Alcohol*	$10^4 k$, litre × × g-equiv.$^{-1}$ s^{-1}
Tetraol (pentaerythritol)	1.68	Diol (propylene glycol)	1.73
Triol (2,2-dimethylbutane-1,1′,1″-triol)	1.86	Triol (glycerol)	1.59

* The alcohol used to initiate polymerisation of propylene oxide is indicated in parentheses.

8. CATALYSIS IN THE REACTION OF ISOCYANATES WITH ALCOHOLS

The question of the mechanism of catalysis in reactions of isocyanates with alcohols is closely interlinked with the problem of the mechanism of catalysis in reactions of other carbonyl compounds [22] on the one hand, and with the activation of alcohols and other hydroxyl compounds [51] on the other. However, apart from the extremely interesting and little studied theoretical aspects of catalysis in the former reactions, the problem is also of great practical importance.

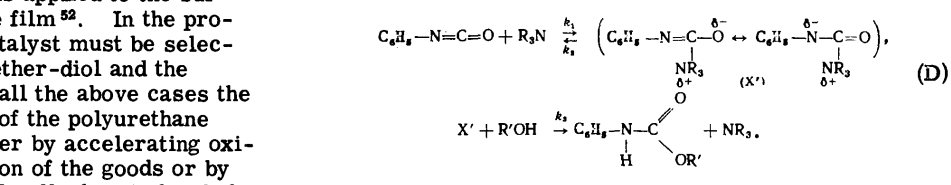
In the choice of industrial catalysts for the manufacture of polyester–urethane rubbers, the requirements which they have to meet depend on the character of the process and its technology. In the moulding of articles directly from the polymer mass, for example, it is necessary that it should retain its plasticity and mobility for a certain time after the reactants have been mixed, and then be converted quite rapidly into the completely vulcanised polyurethane rubber [1]. The requirements are the same in the application of polyurethane films and lacquers: the mixture must remain "lively" from the instant of mixing of the polyol and the di-isocyanate until it is applied to the surface, and then set rapidly to a stable film [52]. In the production of polyurethane foams the catalyst must be selective towards the di-isocyanate–polyether-diol and the di-isocyanate–water reactions. In all the above cases the catalysts should not promote ageing of the polyurethane rubbers obtained with their aid, either by accelerating oxidative degradation or photodegradation of the goods or by catalysing the formation of additional, allophanate bonds by interaction with traces of unchanged isocyanate.

From the above, far from complete list of the varied requirements to be met by the catalysts it is evident that a rational choice thereof can be made only on the basis of systematic combined investigations of the kinetics, the mechanism, and the chemistry of their action. Only a few quantitative studies have been published on the nature and action of catalysts for the reactions of isocyanates.

Although a large number of catalysts have been described, the problem of the mechanism of catalysis, i.e. of why a catalyst enhances the activity of a reactant molecule, remains unsolved. Its solution is complicated by the fact that compounds belonging to different classes, and frequently having directly opposite properties, catalyse the reactions of isocyanates with alcohols. The catalysis of the reactions of isocyanates has several features in common with that of reactions of certain carbonyl compounds, e.g. acid chlorides, anhydrides, esters, etc. In the present case, however, peculiarities are present associated both with the structure of the NCO group and with the fact that in all the above cases nucleophilic substitution is involved, whereas nucleophilic addition occurs in the reactions of isocyanates. Like the hydrolysis and the alcoholysis of certain carbonyl compounds, the reactions of isocyanates are accelerated by bases [53,54]. They are typically catalysed by organic compounds of metals [4], which is less characteristic of carbonyl compounds, but nevertheless has been described in the literature [55]. Acid catalysis, which is very widespread with esters and amides, is not very effective with isocyanates, which makes them akin to acid chlorides. This is apparently associated in both cases with the weak basic character of the compounds. As in the case of acylation with acid chlorides and anhydrides, the addition of alcohols to isocyanates is accelerated by tertiary amines [4,56,57].

Many authors explain the action of a catalyst by the occurrence of complex formation, but it is not sufficient to assume that a catalyst forms a complex with one of the reactants. It is not even sufficient to establish that a complex is in fact formed: many cases are known in which the complexes observed do not take part in the reaction. It is necessary to show that the reaction velocity is proportional to the concentration of a complex formed by the catalyst with one of the reactants. To understand the action of a catalyst, it is very important to ascertain why formation of a particular complex results in enhanced reactivity of a reactant molecule. Catalysts of amine type have been studied the most thoroughly. However, the mechanism by which they catalyse the reaction of isocyanates with alcohols is still not clear.

The possibility that the amine activated both the isocyanate molecule [25,26,58,59] and the molecule of the hydroxyl compound [60–62] has been discussed since the first quantitative work on catalysis [25,26]. In the first case a scheme (D) was proposed [25,26] in conformity with existing views on the catalysis by amines of nucleophilic substitution reactions at a carbonyl group [22]



(D)

As in the case of the catalysis of acylation by acid chlorides [57], it may be supposed that the appearance of the extremely strong electron-attracting substituent $^{+}NR_3$‡ substantially increases the deficiency of electron density on the carbon, while a new electron-donor centre appears. Both factors favour subsequent addition of an alcohol molecule to the complex X″.

The scheme (D) led to the rate equation

$$-dC_{RNCO}/dt = \frac{k_1 k_3 C_{R'OH} C_{RNCO} C_{NR_3}}{k_2 + k_3 C_{R'OH}}, \qquad (9)$$

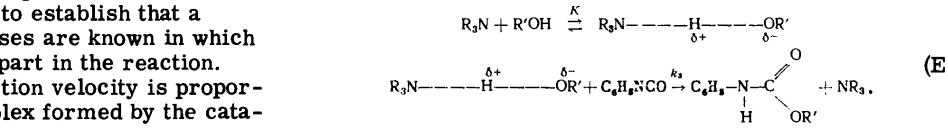
based on the hypothesis of a steady state with respect to the intermediate complex, consumption of the complex being more rapid than its formation. Some authors consider [25,26,58] that the correctness of scheme (D) is confirmed by the fact that the kinetic data give linear plots of $1/k_{cat}$ against $C_{R'OH}$ in conformity with Eqn. (9), where $k_{cat} = k_1 k_3/(k_2 + k_3 C_{R'OH})$ is the catalytic rate constant in the equation for the observed rate constant

$$k_{obs} = k_0 + k_{cat} C_{NR_3}, \qquad (10)$$

k_0 being the rate constant for the uncatalysed reaction. An equation similar to (9) can be obtained also on the hypothesis that equilibrium in the formation of the complex is established rapidly, whereas consumption of the complex is slow

$$-dC_{RNCO}/dt = \frac{K k_3 C_{R'OH} C_{RNCO} C_{NR_3}}{1 + K C_{R'OH}}. \qquad (9')$$

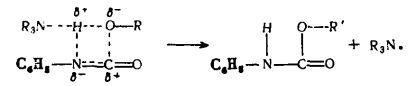
On the basis of scheme (D), however, the slope of the above linear plot should be independent of the nature of the alcohol in both cases, which is not in fact so [25,26]. The sole piece of work [63] in which a complex resembling the postulated intermediate product X′ was supposed to have been detected by infrared spectroscopy proved to be erroneous [47,62]. A fresh discussion has now appeared in the literature of a mechanism of catalysis by amines involving formation of an amine–alcohol complex [62], which then reacts slowly with the isocyanate (scheme E)



(E)

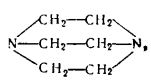
‡ For example, the value of σ^* for $^{+}N(CH_3)_3$ is +5.3, compared with +3.9 and +3.1 for NO_2 and F [37].

The latter reaction may involve formation of a four-membered activated complex[62], e.g.



The kinetic equation for mechanism (E) is identical with Eqn. (9). On the basis of formal kinetic data, therefore, no choice can be made between the two mechanisms. Mechanism (E) is supported by the fact that various amines can form hydrogen bonds with compounds containing OH and SH groups[51,62,64,65]. Formation of such complexes substantially polarises the OH and SH bonds, which is shown in an increase in the dipole moments, the polarisation increasing monotonically with the basic strength of the amine[51]. The formation of hydrogen bonds quite often increases the reactivity of compounds containing hydroxy-groups[66].

Until recently the absence of a direct correlation between the basic strength of an amine and its catalytic activity told against scheme (E). Although increasing basic strength of the amine is usually accompanied by enhancement of catalytic activity, several cases are known in which a feebly basic amine is highly active, and conversely. A linear relationship has been found[59] between the rate constant for the reaction of phenyl isocyanate with 2-ethylhexanol in benzene and the pK_a values of a series of amines. With pentamethylguanidine and 1,4-diazabicyclo[2,2,2]octane (triethylenediamine), however, the rates are respectively an order of magnitude smaller than, and five times as great as, would be expected from their basic strengths. The high catalytic activity of triethylenediamine is connected with its structure



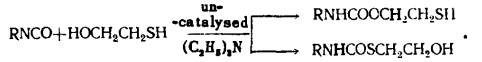
which makes both nitrogen atoms accessible to attack by the isocyanate.

On the other hand, diethylaniline, which has similar basic strength, possesses practically no activity, because the nitrogen atom is strongly screened by the ethyl groups. A similar discrepancy between the basic strength of an amine and its catalytic activity is observed in the catalysis of acylations with acid chlorides[57]. Special experiments have shown that an important part is played in these cases by steric hindrance to the approach of the amine catalyst to the acid chloride. It has been shown[59], however, that the activity of amines with respect to the polymerisation of phenyl isocyanate varies strictly in the sequence of their basic strengths (Table 11), which suggests that steric hindrance to the approach of an amine to the isocyanate is absent. If an amine–isocyanate complex is actually the active complex formed in the first stage of the catalytic reaction (scheme D), steric hindrance should arise only when the alcohol attacks the complex molecule.

According to Flynn and Nenortas[59] mechanism (E) is not consistent with the increase in the isotope effect, with increasing basic strength of the amine, observed in the reaction of phenyl isocyanate with 2-ethylhexanol. These workers consider that, if such a mechanism were operative, increase in basic strength of the amine should be accompanied by an increase in the "detachment" of hydrogen from the alcohol, which should diminish the role of the isotope effect, in contradiction to the results obtained§.

All comparisons between the activity of an amine catalyst and its basic character have been based on the value of pK_a in aqueous solution as a measure of basic strength, although the reaction is carried out in non-aqueous media. Transfer from one solvent to another may change not only the absolute basic strength but also the sequence of amines with respect to this property[68]. In fact, from a comparison of the rate of the catalysed reaction between phenyl isocyanate and 2-ethylhexanol in ethyl acetate, Farkas and Strohm[62] found a correlation between the rate constant k_{cat} and the parameter $E_{\frac{1}{2}}$¶, characterising the basic strength of an amine in this non-aqueous solvent (Table 12). Therefore these workers[62], in agreement with the results of other investigations[60,61], give their preference to scheme (E) in catalysis by amines. It is evident from Table 12 that there is no correlation between k_{cat} and pK_a.

It is interesting that, when an isocyanate reacts with 2-mercaptoethanol, the uncatalysed reaction yields only the *O*-urethane, the *S*-urethane being formed when an amine catalyst is introduced into the reaction medium:



The explanation given[60] for this fact is that the amine interacts preferentially with the more acidic SH group to form intermediate compounds of the type $R_3N\ldots H{-}SCH_2CH_2OH$, with subsequent ionisation of the mercaptoalkanol. Since

TABLE 11. Relative activity of a series of amines in the polymerisation of phenyl isocyanate and in the formation of a urethane in the reaction of phenyl isocyanate with 2-ethylhexanol and the isotope effect in the latter reaction compared with the basic strength of the amine[59].

Amine	pK_a	Catalytic activity in: polymerisation	Catalytic activity in: urethane formation	k^H_{cat}/k^D_{cat}
1,4-Diazabicyclo[2,2,2]octane	8.7	4	2	1.48
1,1,3,3-Tetramethyl-2-*N*-phenylcarbamoylguanidine	10.4	3	3	1.79
Pentamethylguanidine	15.6	2	4	1.96
Heptamethylisobiguanidine	17.1	1	1	2.5

TABLE 12. Comparison of catalytic activity, pK_a value, and basicity in ethyl acetate ($E_{\frac{1}{2}}$) for a series of amines in the reaction of phenyl isocyanate with 2-ethylhexanol[62].

Amine	k_{cat}, g mole^{-1} s^{-1}	Relative activity	pK_a	$E_{\frac{1}{2}}$
Triethylenediamine	5600	1	8.60	124
2-Methyl-1,4-diazabicyclo[2,2,2]octane	5130	0.92	8.86	168
Triethylamine	500	0.19	10.64	186
N-Ethylmorpholine	315	0.05	7.15	291

§ The arguments of Flynn and Nenortas are by no means self-evident. In the reaction of tritiated and light water with triphenylsilane catalysed by bases, for example, the increase in basic strength on passing from pyridine to aqueous–alcoholic alkali results in an increase in k^H_{cat}/k^D_{cat} by a factor of 2.3[67].

¶ According to Hall[69] the basic strength of an amine in a non-aqueous medium is measured by the position of the point of inflection on the curve for potentiometric titration with perchloric acid (72% $HClO_4$ in dioxan), expressed in millivolts — $E_{\frac{1}{2}}$.

$HOCH_2CH_2S^-$ is more basic than $HSCH_2CH_2OH$, reaction in the presence of a catalyst yields the *S*-urethane.

It must be noted that the concept of catalysis as a result of activation of an OH or SH bond by hydrogen bonding leaves it obscure why only amines and a few oxygen compounds which do not possess a high donor ability — tetrahydrofuran, dioxan, and ethers — should exhibit catalytic properties. In the relationship between the basicity constants of substances and their capacity for hydrogen bonding there is usually no qualitative difference between nitrogen and oxygen compounds[70], which simply arrange themselves one after the other in the sequence of their basic strengths. Nevertheless, transfer from hydrocarbon solvents to ethers, dioxan, and tetrahydrofuran[28] is accompanied by a sharp drop in reaction velocity, which is clearly caused by the formation of hydrogen bonds.

Organometallic compounds and metal salts have recently begun to be widely used as catalysts for the reactions of isocyanates. They include, for example, alkyl carboxylates and alkyl halides of Sn^{IV} (dibutyltin diacetate, dibutyltin dichloride, etc.); octanoates, stearates, and naphthenates of Cr^{III}, Ni^{II}, Zn^{II}, Bi^{III}, Fe^{III}, Sn^{II}, etc.; and acetylacetonates of Fe^{III}, Pb^{II}, Cu^{II}, Mn^{III}, Co^{II}, etc. A quite full analysis of published data will be found in papers by Farkas and Mills[4] and by Robins[71]. Table 13 gives for comparison the relative catalytic activities of two typical catalysts of different classes.

Organometallic compounds are more active by factors of 10^2–10^4 than amine catalysts of average activity. Although a large number of organometallic catalysts have been described[72–74], there is as yet no generally accepted view of the nature of their catalytic action. Again, the possibility has been discussed that a complex may be formed with the isocyanate[75], with the alcohol[76], and with both components[71,72,77]. Results have been published on the changes undergone by the spectral characteristics of isocyanates and alcohols when metal-containing catalysts are added to the system. For example, cobalt stearate[77] and cobalt octanoate[75] form with phenyl isocyanate complexes which are apparent in the infrared and ultraviolet spectra. Moreover, the catalytic activity of cobalt octanoate increases when it is kept mixed with phenyl isocyanate in toluene for 20 min or longer[75], which suggests the slow formation of an active product.

Recent results indicate[78] that tin compounds containing the Sn–O bond, e.g. R_3SnOR', readily add on to isocyanates and isothiocyanates to form carbamates containing tin:

$$(C_4H_9)_3SnOCH_3 + C_6H_5{-}N{=}C{=}O \rightarrow (C_4H_9)_3Sn{-}N(C_6H_5){-}COOCH_3.$$

Bloodworth and Davies suggest a mechanism of catalysis by organotin compounds of the reaction between isocyanates and alcohols, based on the fact that the above compounds readily react with alcohols to form urethanes. In the first stage any tin(IV) compound gives with an alcohol R'OH or phenol present in the system a tin alkoxide R_3SnOR'. This is followed by the reactions

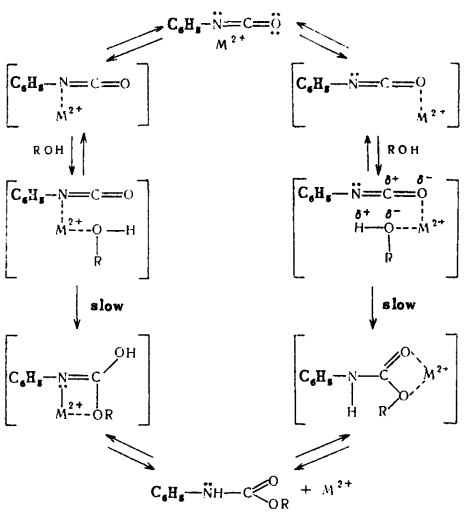
$$R_3SnOR' + C_6H_5{-}N{=}C{=}O \rightarrow R_3SnN(C_6H_5)COOR',$$
$$R_3SnN(C_6H_5)COOR' + R'OH \rightarrow R_3SnOR' + C_6H_5NHCOOR'.$$

However, the absence of quantitative data, on the basis of which the rates of known catalytic reactions could have been compared with those of the reactions suggested by these workers[78], makes it impossible either to accept or to reject this mechanism.

Observations have been made also on the activating effect of a metal-containing catalyst on the alcoholic component of the reaction mixture. For example, Blagonravova et al.[76] found that preliminary treatment of 2-hydroxyethyl adipate with zinc oxide or an acetate of this or several other metals activates the diol by forming an alkoxide. The sequence of activities is as shown in Table 14.

Complex formation between an organometallic catalyst and an alcohol is indicated also by an examination of the proton magnetic resonance spectra. According to Frisch et al.[47] 0.05–0.855 M dibutyltin dilaurate produces a substantial chemical shift (δ from 2.56 to 3.99 p.p.m.) of the hydroxyl proton in 1-methoxypropan-2-ol dissolved (0.54 M) in carbon tetrachloride, the value of δ being proportional to the concentration of tin(IV). Zabrodin and ourselves[79] have obtained similar results from an investigation of the proton resonance spectra of solutions of methanol in carbon tetrachloride in the presence of di-n-butyltin diacetate and dilaurate.

Several authors have concluded[71,72,77] that the active species is a ternary equilibrium complex containing the catalyst, the isocyanate, and the alcohol. Robins[71] puts forward two schemes for the formation of an active ternary complex of this type, of which scheme (F) applies to simple alcohols:



(F)

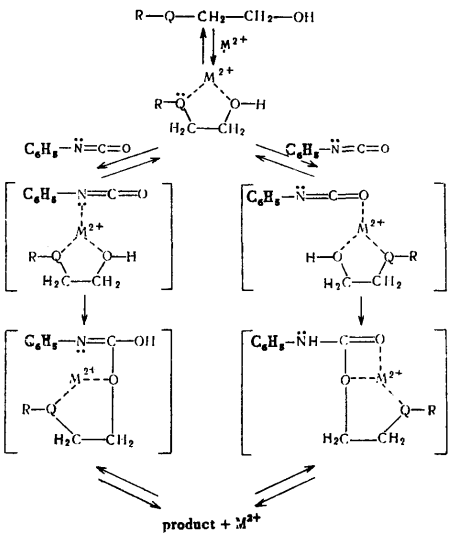
TABLE 13. Comparison of activities of triethylamine and di-n-butyltin diacetate as catalysts in the reaction of phenyl isocyanate with methanol in dioxan as solvent (Ref. 4, p. 421).

Catalyst	Concn., mole %	$10^4 k$, litre mole^{-1} s^{-1}
No catalyst	—	0.51
Triethylamine	1	6.7
Di-n-butyltin diacetate	0.009	118.0

TABLE 14. Comparison of catalytic activities of acetates of various metals[76].

Acetate	Activity	Acetate	Activity
K	3.45	Cu	0.90
Na	2.49	Ca	0.64
Co	1.20	Mg	0.53
Zn	1.00		

When the alcohol contains an "active" donor group Q in the α-, β-, or γ-position with respect to the hydroxy-group, the scheme of the reaction appears as follows:



(G)

In effect, neither mechanism is based on any strict evidence, but merely on general considerations relating to the structure of the reactants and on qualitative data on the activities of a series of catalysts, containing metal atoms or ions, towards isocyanates and alcohols of various structures.

In conformity with the above schemes, Robins formulates the following requirements to be satisfied by an organometallic catalyst: (*a*) it must possess some minimum capacity for complex formation in order that an adequate concentration of the ternary complex shall be maintained; (*b*) it should not suppress the nucleophilic character of the alcoholic oxygen, at any rate not sufficiently to make the reaction improbable; and (*c*) it should not yield with the reaction products a stable complex, which would make departure of the metal ion from the reaction zone improbable.

To obtain quantitative data on the alcohol–isocyanate reaction catalysed by tin(IV) compounds, we have recently made a detailed kinetic study of the reaction between methanol and *p*-chlorophenyl isocyanate in heptane in the presence of a series of tin compounds (di-n-butyltin diacetate, dilaurate, and dichloride)[79-82]. The rate of the catalytic reaction was shown (Fig. 2) to be proportional to the concentration of the alcohol–catalyst complex, which was determined independently by a spectroscopic method. Experiments on the thermodynamics of complex formation showed it to be an equimolecular complex. The equilibrium constant, heat of reaction, and entropy of complex formation were determined.

The equation for the reaction, deduced on the assumption that the equilibrium

$$Sn^{IV} + ROH \overset{K}{\rightleftharpoons} ROH \cdot Sn^{IV} \qquad (11)$$

was established, with a slow bimolecular interaction between the complex and the isocyanate

$$ROH \cdot Sn^{IV} + R'NCO \xrightarrow{k} R'NHCOOR + Sn^{IV}, \qquad (12)$$

satisfactorily reproduces the kinetic data obtained over wide ranges of temperature and concentration:

$$w_{cat} = k_{cat} C_{R'NCO} C_{Sn^{IV}}, \qquad (13)$$

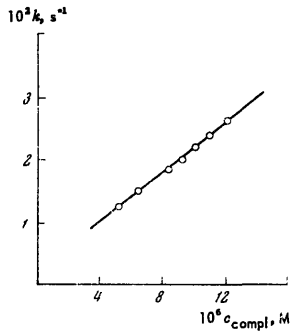


Fig. 2. Dependence of rate constant for the reaction of *p*-chlorophenyl isocyanate with methanol in heptane in the presence of di-n-butyltin dilaurate at 25° on the concentration of the alcohol–catalyst complex.

where w_{cat} is the rate of the catalytic reaction, and

$$k_{cat} = C_{ROH} k K / (1 + K C_{ROH}). \qquad (14)$$

It is seen from Eqn. (14) that both k and K can be evaluated from a plot of $1/k_{cat}$ against $1/C_{ROH}$. The complex formation constants K found from the kinetic data agree, within the limits of experimental error, with those measured directly. Values of k and K are listed in Table 15.

From the temperature dependence of k and K, values were obtained of $E = 6.7 \pm 0.5$ kcal mole^{-1} and $\Delta S^{\neq} = -23.7$ cal mole^{-1} deg^{-1}, and also the heat and the entropy of complex formation $\Delta H_{compl} = -1.3 \pm 0.5$ kcal mole^{-1} and $\Delta S_{compl} = -3.2 \pm 1.0$ cal mole^{-1} deg^{-1}. Within the limits of experimental error, the latter two values are close to the corresponding values, -0.9 ± 0.5 kcal mole^{-1} and -1.2 ± 1.0 cal mole^{-1} deg^{-1}, found directly from spectrophotometric data on complex formation between dibutyltin dilaurate and methanol.

The results obtained show that introduction of a catalyst increases the rate constant for the step involving interaction between isocyanate and alcohol, by a factor of about 10^6 in comparison with the uncatalysed reaction. Comparison of the kinetic parameters for the uncatalysed and the catalysed reactions of *p*-chlorophenyl isocyanate with methanol shows that decrease in the activation energy from $E_{uncat} = 8.2$ kcal mole^{-1} to $E_{cat} = 6.7$ kcal mole^{-1} results in an increase in rate by a factor of about 10, the main acceleration of the process (by a factor of 10^5) being a result of a sharp decrease in the negative entropy of activation from $\Delta S^{\neq}_{uncat} = -44.5$ cal mole^{-1} deg^{-1} to $\Delta S^{\neq} = -23.7$ cal $\times$ $\times$ mole^{-1} deg^{-1}: i.e. the structural requirements when the reactants approach one another in the reaction step become less rigorous. Since in our experiments the reaction medium was n-heptane, solvation phenomena played little part in the variation in $\Delta S^{\neq}$, everything being determined by the structure of the activated complex. In the uncatalysed reaction, in which a four-membered activated complex is formed in a single step, rigid limitations are imposed on the mutual disposal of isocyanate and alcohol molecules, which is reflected in the large negative entropy of activation.

Table 15 shows that the constant K, determined from kinetic data, did not change on passing from *p*-chlorophenyl to phenyl and *m*-chlorophenyl isocyanates. This provides further confirmation that only the alcohol is involved in the complex formation which is active in catalysis.

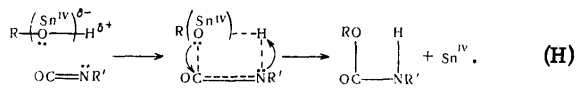
TABLE 15. Temperature dependence of k and K for various phenyl isocyanates.

T, °K	$10^3 k$, litre mole^{-1} × ×s^{-1} p-chlorophenyl	K, litre mole^{-1} p-chlorophenyl	K, litre mole^{-1} phenyl	K, litre mole^{-1} m-chlorophenyl
25	1.26	5.9	5.9	5 6
35	1.76	5.5	—	—
45	2.56	5.1	—	—

Since a specific feature of quadrivalent tin compounds is their ability to form donor–acceptor complexes, it may be supposed that the active intermediate product in the catalytic reaction between isocyanate and alcohol is formed by vacant 5*d*-orbitals of the tin and the lone pair of electrons on the basic oxygen of the alcohol. Apparently the main result of interaction between alcohol and organotin catalyst which accelerates the reaction is a change in properties of the hydroxy-group: firstly, the dipole moment of the bond is increased by the redistribution of electron density accompanying complex formation, and such redistribution can be a consequence not only of the formation of an O–Sn bond but also of the presence of conjugation between vacant 5*d*-shells of the tin and a free pair of 2*s*-electrons of the alcoholic oxygen not involved in formation of the O–Sn bond; secondly, the OH bond is lengthened by the diminution in the density of the cloud of valency electrons.

It is still too early to specify the mechanism of the reaction between the alcohol–catalyst complex and the isocyanate, but two probable routes can be imagined for the interaction.

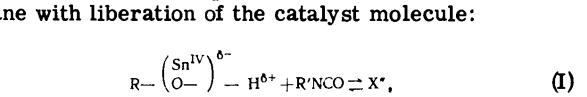
1. Reaction takes place in a single step with simultaneous transfer of a lone pair of electrons from the isocyanate nitrogen atom to the alcoholic proton and from the alcoholic oxygen to the isocyanate carbon[18–20]:



(H)

With this reaction mechanism, lengthening the OH bond and bringing it close to the C=N bond length in the isocyanate group (1.18 Å) should substantially facilitate formation of the four-membered activated complex and lower the absolute value of the negative entropy of activation.

2. Reaction takes place in stages. In the first stage the isocyanate is attacked by the alcoholic proton in the complex with formation of an intermediate product X″, which is ionic or polar in nature. The bond thus formed results in substantial activation of the carbonyl carbon in the product X″ by the appearance on it of a deficiency of electron density, and hence a fractional positive charge. The alcoholic oxygen is still firmly bound to the tin of the catalyst. In the second stage, as a result of detachment of the alcoholic oxygen from the tin and its transfer to the carbon of the isocyanate, which has already added on a proton, the intermediate product X″ is converted into a urethane with liberation of the catalyst molecule:



(I)

With such a two-stage mechanism, involving the intermediate formation of linear activated complexes, the entropy of activation should be considerably less negative than in the case of the uncatalysed reaction.

It is as yet difficult to tell which of these schemes operates during the reaction. However, examination of either of them leads to the extremely interesting conclusion that the reaction rate constant depends on the equilibrium constant of the intermediate complex. In the above cases the reactivity of the alcoholic hydrogen should increase with the stability of the complex. On the other hand, increase in its stability will diminish the nucleophilic character of the oxygen, and thereby diminish its reactivity towards the isocyanate carbon. If these views on the reaction mechanism are correct, both a considerable increase in stability of the complex and a considerable decrease should lower the rate constant of the catalytic reaction. The most active catalysts should be those which form complexes of optimum stability, characterised by definite values of the equilibrium constant.

The presence of a maximum in the activities of the series of catalysts investigated (Fig. 3) provides still further support for our hypothesis on the nature of the catalytic effect of organotin compounds in reactions between isocyanates and alcohols.

Complex formation between an organotin compound and an alcohol results in increased mobility of the hydroxyl hydrogen and an enhancement of its electrophilic activity towards the NCO group.

In the case of a catalytic reaction of this type, a change in the mechanism of addition is apparently to be expected, from nucleophilic to electrophilic. Such a change should be accompanied by a decrease in the absolute magnitude of the parameter $\rho > 0$ in the Hammett equation on passing from the non-catalytic to the catalytic reaction. Fig. 4 shows the dependence of $\log(k/k_0)$ on σ for a series of substituted phenyl isocyanates. It is seen that actually the value of $\rho = 0.9$ for the reaction catalysed by di-n-butyltin dilaurate, which is significantly less than the value of 3.3 for the uncatalysed reaction. The sign of ρ may be expected to change on passing to stronger acceptors.

An important but very little studied problem in the reactions of isocyanates is that of acid–base catalysis. Almost

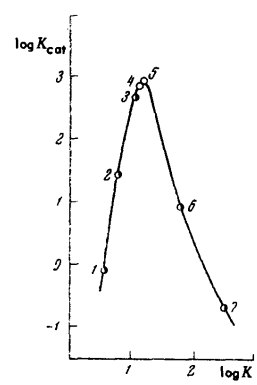


Fig. 3. Correlation between catalytic activity of catalysts and stability of their complexes formed with methanol:
1) $(C_2H_5)_4Sn$; 2) $(C_2H_5)_3SnCl$; 3) $(C_2H_5)_2SnCl_2$; 4) $(CH_3COO)_2Sn(C_4H_9)_2$; 5) $C_{11}H_{23}COO)_2Sn(C_4H_9)_2$; 6) $C_2H_5SnCl_3$; 7) $SnCl_4$.

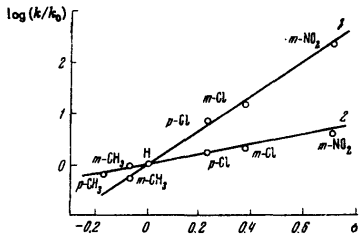


Fig. 4. Dependence of log (k/k_0) on Hammett σ-parameter for reactions of derivatives of phenyl isocyanate with methanol in heptane at 25°:
1) uncatalysed reaction; 2) in the presence of di-n-butyltin dilaurate.

all known papers on the influence of acids and bases on the reactions of isocyanates are cited in the review by Farkas and Mills[4]. The lack of quantitative data makes it difficult to give soundly based judgments on the mechanism. The most complete qualitative picture of the effect of acids and bases on the reactions of isocyanates has been described by Heiss et al.[53] These workers showed that the reaction is accelerated by the addition of basic reagents, including sodium and potassium hydroxides, sodium phenoxides, trisodium phosphate, benzyltrimethylammonium hydroxide, etc. The retarding action of small additions of acids to previously "purified" polyetherdiols is apparently merely the result of neutralisation of remaining traces of bases. The correctness of this view was demonstrated by the fact that, with reagents which had been completely freed from alkali, e.g. ethylene glycol and cyclohexanol, addition of acid produced no observable retarding effect. With higher concentrations (> μ-equiv. g^{-1} oligomer) a slight accelerating effect is observed.

The boron trifluoride–ether complex also slightly accelerates the reaction of butanol with phenyl isocyanate. Sharp intensification of the catalytic action of boron trifluoride[48] and of zinc chloride[49] occurs on passing to nitro-alcohols, and this can be understood on the basis of the mechanism (H)–(I) suggested above: the strong acceptor boron trifluoride yields with butanol such a stable complex that it is difficult to transfer the combined oxygen to the isocyanate by reaction (12). The substantial decrease in basic strength on passing to nitro-alcohols produces an alcohol–catalyst complex of diminished stability and "moves" the reaction system into a region of higher catalytic activity (cf. Fig. 3). The same applies also to zinc chloride.

The catalytic action of alkalis on the reaction of an alcohol with an isocyanate can again consist either in activation of the OH bond of the alcohol by inducing a hydrogen bond

$$ROH + OH^- \rightleftarrows \overset{\delta-}{RO}\text{–}H \ldots \overset{\delta-}{OH},$$

or even in formation of an alkoxide ion

$$ROH + OH^- \rightleftarrows RO^- + H_2O.$$

Activation of the isocyanate group is also possible, with formation of an intermediate ion Y^- analogous to the ion suggested by Zahradník[24] for isothiocyanates:

$$RNCO + OH^- \rightleftarrows R\bar{N}\text{–}C(=O)(OH) \leftrightarrow RN{=}C(O^-)(OH) \quad (Y^-),$$

followed by an addition–substitution reaction occurring either in one stage

$$Y^- + ROH \rightarrow R\text{–}\overset{\delta+}{H}\text{---}\overset{\delta-}{O}R\text{–}N\text{–}C{=}O \rightarrow R\text{–}N(H)\text{–}C(OR){=}O + OH^-.$$

or in two stages with formation of an intermediate ion Z^-

$$Y^- + ROH \rightarrow RNH\text{–}C(OR)(O^-) \rightarrow RNH\text{–}C(OR){=}O + OH^-.$$

The study of catalysis by strong acids is complicated by the occurrence of secondary addition reactions. Sulphuric acid, for example, forms derivatives of sulphamic acids with isocyanates[83], carbon dioxide being evolved. It can definitely be stated, however, that an alcohol is so much more basic than an isocyanate that, at low acid concentrations, only the protonated form of the alcohol ROH_2^+ will be present even in non-aqueous solvents. Protonation of RNCO will be practically completely absent. It may therefore be supposed that, under the conditions described in the literature[4,53], alkyloxonium ions will constitute the active form.

In the range of acidities in which RNCO begins to be protonated, practically the whole of the alcohol will be in the ionic form. It is still possible, however, that the formation of small amounts of extremely active intermediate protonated forms of the isocyanate U^+ will result in acceleration of the reaction:

$$H^+ + R\text{–}NCO \rightleftarrows \begin{cases} RNH\text{–}\overset{+}{C}{=}O \\ RN{=}\overset{+}{C}\text{–}OH \end{cases} \quad (U^+),$$

$$U^+ + R'OH \longrightarrow RNHCOOR' + H^+.$$

Since only unprotonated alcohol molecules should take part in the latter reaction, and their concentration will fall with increase in acidity, an extremal dependence of the reaction velocity on the acidity of the medium should be observed, and should be found at higher acid concentrations the less basic the alcohol. In the case of acid-catalysed reactions, protonation of the isocyanate will be favoured by a substituent of nucleophilic character adjacent to the NCO group and in the ring of the phenyl isocyanate.

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FLUORIDES OF HIGH OXIDISING POWER AND THEIR APPLICATION TO THE PREPARATION OF ORGANIC FLUORINE COMPOUNDS

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I. INTRODUCTION

The extraordinarily high reactivity of elementary fluorine, together with the chemical properties of organic fluorine compounds, make methods for synthesising the latter fundamentally different from those for obtaining other halogen derivatives. All methods of preparing organic fluorine compounds can be divided into four broad groups.

The first group comprises reactions of organic compounds with elementary fluorine or with fluorides of high oxidising power. These reactions are essentially oxidations, taking place by a radical mechanism, and involving either replacement of hydrogen (or halogen) by fluorine or addition of fluorine to a multiple bond.

The second group is formed by reactions involving the exchange of other halogens for fluorine by means of hydrogen fluoride or a metal fluoride possessing no oxidising power (potassium fluoride, antimony trifluoride).

In the third group of reactions functional groupings containing oxygen, sulphur, or nitrogen are exchanged for fluorine by interaction with sulphur tetrafluoride, by the Schiemann reaction, and by other methods.

The fourth group can be regarded as including the numerous reactions in which groupings containing fluorine are introduced into organic compounds containing no fluorine, by the scheme

$$R_H - X + R_F Z \rightarrow R_H - R_F + XZ,$$
$$R_{H(\text{or } F)} - CH = CH_2 + R_F - X \rightarrow R_H - \underset{\displaystyle X}{\underset{|}{CH}} - CH_2 - R_F.$$

The present review will cover only reagents which effect reactions of the first group, i.e. fluorides which oxidise organic compounds to organofluorine compounds. Attention will be paid primarily, not to summarising the extensive literature on the most important fluorinating agents (AgF_2, CoF_3), but to elucidating the theoretical possibility of using fluorides for this purpose as a function of the chemical properties of the element concerned and its position in the Periodic System. Higher fluorides of the transition metals and of certain elements in the main subgroups of the Periodic System are of great practical importance (in the atomic industry, as oxidants in rocket technology). Information on the fluorides of interest to us will be reported in the sequence in which the elements are arranged among groups of the Periodic System (the elements capable of forming fluorides having high oxidising power are V, Cr, Mn, Tc, Re, Ru, Os, Ni, Pd, Pt, Cu, Ag, Au, Hg, Tl, Pb, Sb, Bi, O, Po, Cl, Br, I, At, Kr, Xe, Rn, Ce, Pr, Nd, Tb, Dy, U, and Pu).

The oxidising power of these fluorides is extremely varied, and cannot yet be estimated quantitatively in any way. Considerable interest should attach, in connection with the assessment of the oxidising power of ElF_x, to the energy of formation of the El–F bonds, but unfortunately knowledge of these bond energies and of their orders is very far from what could be desired. Yet even in such a simple molecule as F_2 the order of the F–F bond is less than unity, which entails an abnormally low bond energy. The reason for such anomaly in this case has been analysed in detail by the molecular orbital method[1]. Some elements are not at all readily available, and therefore have been insufficiently investigated; while others, although readily available, have higher fluorides which cannot be purified, so that their study is difficult. The highly corrosive nature of some fluorides, which attack even polytetrafluoroethylene and platinum, make it impossible to study them by the usual methods. In this paper the assignment of some fluorides to the category of oxidising agents is made on the basis of their chemical properties, often studied quite superficially, and in some cases only on the basis of general considerations regarding their reactivity. Nevertheless, we feel that future quantitative results will hardly seriously contradict our purely qualitative considerations.

Fluorides of high oxidising power show increased stability and lower oxidising power on complex formation, which makes it possible to obtain fluorides in which the metals exhibit an abnormally high valency (Ni^{4+}, Cu^{4+}).

II. HIGHER FLUORIDES OF TRANSITION METALS

Incomplete electron levels become filled in the atoms of transition metals, which comprise elements of atomic numbers 21–30, 39–40, and 57–90 (lanthanum, lanthanides, and the series of elements from Hf to Hg), together with 89–104 (Ac, Th, Pu, U, etc.). Transition metals can utilise the electronic levels *d* (and *f* in the lanthanides and actinides) for chemical bond formation.

Fluorides of high oxidising power occur among quadrivalent derivatives of cerium, praseodymium, terbium, and dysprosium in the lanthanide subgroup of Group III in the Periodic System, and are represented by the hexafluorides of uranium, neptunium, and plutonium in the actinide subgroup.

Whereas in the vanadium subgroup only vanadium pentafluoride possesses high oxidising power, and in the zinc subgroup only mercury difluoride, in the case of chromium, manganese, iron, cobalt, nickel, and copper subgroups only iron gives no fluoride of high oxidising power.

1. Higher Fluorides of Lanthanides

The appearance in lanthanides of 4*f*-electrons, at energy levels close to those of 5*d*-electrons, makes it possible for some lanthanides to yield more or less stable quadrivalent derivatives. The stability of the quadrivalent state diminishes with increase in the number of *f*-electrons, but after $4f^7$-electrons have accumulated in gadolinium, the possibility of forming a relatively unstable quadrivalent state reappears with terbium and to some extent dysprosium.

Cerium and terbium tetrafluorides are obtained by fluorinating the trifluorides with elementary fluorine at high temperatures[2,3]. There are indications that cerium tetrafluoride can be obtained also from the trichloride[4] or the dioxide[5]. Data have been published on the lattice structures of CeF_4 and TbF_4 and on the partial pressures of fluorine over these compounds at high temperatures[3,6].

When heated in air, cerium and terbium tetrafluorides are converted into oxides. The fluorides are unchanged by cold water[2,3], but react quite rapidly even in acidified solutions of aluminium nitrate with the evolution of gaseous oxygen, TbF_4 reacting slowly even in the absence of acid[3].

Fowler used CeF_4 for the vapour-phase fluorination of hydrocarbons with the aim of obtaining perfluorinated products. Since CeF_4 was less reactive than CoF_3, fewer carbon–carbon bonds underwent cleavage, so that more viscous products of higher boiling point were obtained[9]. In the opinion of Fowler and Anderson, CeF_4 is to be preferred to other fluorinating agents if the carbon skeleton is to be obtained unchanged in vapour-phase fluorination over the temperature range 150–450°. There are indications of the use of CeF_4 to obtain partly fluorinated organic compounds[5], and of the addition of fluorine to double bonds in chlorinated alkenes by means of CeF_4.[5] The chlorine in saturated chlorofluorocarbons can be replaced under the influence of CeF_4.[5] Cerium tetrafluoride is employed for the liquid-phase stabilisation of fluorinated oils in the presence of elementary fluorine[5].

It has not yet proved possible to prepare tetrafluorides of other lanthanides[3,10,11], although it has been predicted[12] that praseodymium tetrafluoride will be relatively stable.

Fluoro-complexes are known of quadrivalent cerium[13] and praseodymium[14,15] of general formulae A_2BF_6 and A_3BF_7 (where A = Na, K, Rb, and Cs and B = Ce, Pr), and the compounds $NaPrF_5$,[16] Cs_3TbF_7,[18] Cs_3DyF_7, and Cs_3NdF_7 [18] have also been obtained. In all cases the stability of the complexes increases in the sequence Na → K → Rb → Cs. The lattice parameters and the magnetic suceptibilities of these complexes have been measured[13,14]. All these complexes have been prepared by fluorinating a mixture of salts[16] or a mixture of chlorides and the corresponding oxides[13–15,17] at high temperatures. The cerium complexes are colourless and comparatively stable, and begin to react only gradually with water and hydrochloric acid. They oxidise acidified solutions of potassium iodide; concentrated sodium hydroxide solution decomposes the complexes, with precipitation of $CeO_2.xH_2O$.[13] The colourless praseodymium complexes are reduced by water with gas evolution, and are even decomposed by moist air[14]. As was to be expected, the colourless complex of quadrivalent terbium is somewhat more stable, and does not break down in moist air, but it oxidises boiling hydrochloric acid with the evolution of chlorine. Concentrated NaOH solution decomposes Cs_3TbF_7.[17] Study of the magnetic properties and the elementary composition has proved the existence of the complexes Cs_3NdF_7 and Cs_3DyF_7.[18] The yellow complexes of Nd^{4+} and Dy^{4+} liberate iodine from acidified potassium iodide solution[18].

2. Higher Fluorides of Uranium, Neptunium, and Plutonium

The fact that 5*f*-electrons are considerably more readily removed than are the 4*f*-electrons of lanthanides makes the achievement of high valencies a characteristic feature of actinides. Thus the most stable state of thorium is quadrivalent, protactinium reaches the quinquevalent state, and uranium, neptunium, plutonium, and americium are characterised by sexivalent states. As the number of 5*f*-electrons rises, their tendency to form high valency bonds falls, and the higher valency states become less stable. Thus whereas uranium hexafluoride is fairly stable, although it is a strongly oxidising compound, plutonium hexafluoride is considerably less stable, and exhibits extremely high oxidising power, while americium hexafluoride has not yet been obtained[19]. The immense practical value of the fluorides of uranium and plutonium has resulted in an extensive literature on this question[20–22]. We shall therefore confine ourselves to a brief comparison of the properties of the hexafluorides of uranium, neptunium, and plutonium, and discuss their reactions with organic compounds. The ability of uranium hexafluoride to react with all the usual organic compounds, and the need to produce resistant materials, led to the synthesis of polytetrafluoroethylene, polychlorotrifluoroethylene, and perfluorinated oils, and was the principal reason for the vigorous development of organofluorine chemistry.

Uranium hexafluoride is a moderately strong oxidant, and can be prepared, without the use of elementary fluorine or fluorides of halogens, cobalt, or silver, by the reaction[23]

$$2UF_4+O_2=UF_6+UO_2F_2.$$

Neptunium hexafluoride[24] and especially plutonium hexafluoride[24–27] are stronger oxidising agents. Thus the latter fluorinates bromine trifluoride to bromine pentafluoride[24,27], whereas uranium hexafluoride can be obtained by treating uranium compounds with bromine trifluoride[23].

Plutonium hexafluoride readily fluorinates uranium derivatives to the hexafluoride[27]. Neptunium hexafluoride occupies an intermediate position, only partly converting bromine trifluoride into the pentafluoride[24]. All the hexafluorides are immediately hydrolysed by water, but no evolution of oxygen or oxygen difluoride was observed[28,29]. Uranium hexafluoride reacts vigorously with most organic compounds (aliphatic and aromatic hydrocarbons, alcohols, and ethers) with the evolution of hydrogen fluoride and the formation of partly carbonised substances of indeterminate composition, the uranium being converted into its tetrafluoride or oxide fluoride. Trichloroethylene instantaneously reduces uranium hexafluoride to the tetrafluoride, being converted into a mixture of compounds containing chlorine and fluorine, formed by reactions involving addition, substitution, polymerisation, and decomposition[30].

At 100–200° uranium hexafluoride is rapidly and quantitatively reduced by carbon tetrachloride to uranium tetrafluoride[31]:

$$UF_6+2CCl_4 \rightarrow UF_4+Cl_2+2CCl_3F.$$

This reaction has been carefully studied for its practical application[31]. Experiments with different proportions of the reactants showed that chlorotrifluoromethane predominated when a slight excess of carbon tetrachloride was used, whereas more trichlorofluoromethane was obtained with a large excess.

When uranium hexafluoride is dissolved in 1,1,2,2,-tetrafluoroethane, reaction becomes appreciable only after a few days. The relative stability of this solution permitted its use to study several reactions of uranium hexafluoride with ammonia and with arsenic trifluoride[20]. A solution of uranium hexafluoride in tetrachloroethane is still more stable[20]. This solution takes a few weeks to decompose, and can be used for the recrystallisation of uranium hexafluoride. On the other hand, tetrachloro-1,2-difluoroethane reacts with uranium hexafluoride quite rapidly, with the evolution of a gas which is obviously dichlorodifluoromethane[20].

Uranium hexafluoride reacts with partly fluorinated hydrocarbons, replacing the hydrogen by fluorine atoms, but is completely inert towards perfluorinated hydrocarbons and chlorofluorocarbons, which are used in various operations with the hexafluoride. On prolonged heating, amorphous carbon reduces uranium hexafluoride to the tetrafluoride, with the formation of carbon tetrafluoride and other simple fluorocarbons. The hexafluoride is insoluble in carbon disulphide, and reacts relatively slowly; with moist carbon disulphide, fluorides of sulphur are formed. Uranium hexafluoride does not interact with carbon dioxide or with mercury dicyanide[20].

Plutonium hexafluoride reacts with most organic compounds still more vigorously, but perfluorinated hydrocarbons do not interact with it, too[27].

3. Higher Fluorides of the Vanadium Subgroup

Elements of this subgroup are characterised by the presence of relatively few *d*-electrons, whose energy levels are close to those of the valency *sp*-electrons. This results in participation by the *d*-electrons in the formation of valency bonds, as a result of which the elements of the vanadium subgroup exhibit a stable higher valency of +5. With increase in atomic number the mobility of the *d*-electrons increases; this tends to stabilise the higher valency of the element. In the series vanadium–niobium–tantalum the larger the positive charge on the nucleus the more weakly are the outer electrons bound to the nucleus, the lower is the ionisation potential for detachment of the corresponding electrons, and the greater the tendency of the element to form compounds corresponding to its maximum valency. The higher fluorides of elements of this group are oxidants, their oxidising power diminishing down the group.

Vanadium pentafluoride is formed by the action of fluorine on the metal at 300°,[32] by the action of chlorine trifluoride, bromine trifluoride, or iodine pentafluoride on vanadium pentoxide[33], or by the thermal disproportionation of vanadium tetrafluoride at 650°.[32] It is a relatively weak oxidising agent, but can exchange fluorine for oxygen in inorganic compounds and for other halogens in carbon tetrahalides[34,35]. There are indications that vanadium pentafluoride reacts with ether and with toluene, but the structure of the products has not been elucidated[32]. It forms salts with ammonia and with pyridine[36]. Niobium and tantalum pentafluorides are less active as oxidising agents[35].

4. Fluorides of Chromium, Molybdenum, and Tungsten

For a long time chromium hexafluoride was not identified. Fowler and his coworkers tried to obtain higher fluorides of chromium by the interaction of fluorine with chromium trichloride and chromium sesquioxide in order to study their ability to fluorinate organic compounds, but only a mixture of volatile and non-volatile fluorides was obtained, which could not be investigated because of experimental difficulties[37]. Bright red chromium pentafluoride[39] has recently been obtained, together with a small quantity of lemon-yellow chromium hexafluoride[38], by treating chromium powder with fluorine in a nickel bomb at 200 atm and 400°.[38] The yield of the hexafluoride is increased by adding manganese powder and raising the pressure to 350 atm. Chromium hexafluoride rapidly decomposes into the pentafluoride and fluorine at temperatures as low as -100° to -80°.[38]

Molybdenum and tungsten hexafluorides, in contrast, are readily available, but exhibit relatively weak oxidising properties and have no fluorinating action[40,41]: with organic compounds they form complexes.

5. Fluorides of Manganese and Rhenium

The presence of a large number of *d*-electrons enables elements in this subgroup to exhibit various valencies (+2, +3, +4, +6, and +7), the higher valencies becoming more stable from manganese to rhenium. Manganese forms a trifluoride and a tetrafluoride. The former has been well studied, and has found practical application as an extremely effective fluorinating agent (though milder than cobalt trifluoride) for organic compounds. Manganese trifluoride is used for the preparation of perfluorinated compounds under roughly similar conditions to cobalt trifluoride, the latter being more suitable for the fluorination of products of low boiling point, whereas manganese trifluoride is more useful for high-boiling compounds, since at high temperatures it causes less cleavage of carbon–carbon bonds, though the resulting product is probably incompletely fluorinated[42–45].

Wine-red manganese trifluoride is formed by treating manganese or its salts with fluorine at 250° or by treating

manganese iodate with bromine trifluoride and heating the product to 200°.[46] The extremely active manganese tetrafluoride is obtained under more severe conditions, by fluorinating simple salts ($MnCl_2$, MnF_2, $MnSO_4$,[47] MnF_3[48]) with elementary fluorine at 400–550°. The tetrafluoride is an amorphous powder, which is fairly stable at room temperature[48].

Manganese tetrafluoride is undoubtedly more reactive than the trifluoride. The latter is decomposed by water, whereas the tetrafluoride ignites spontaneously on contact with water. The trifluoride reacts with benzene, alcohol, chloroform, ether, and turpentine only when heated to 100° and above[49]. A flash of light is seen when the tetrafluoride reacts with dry petroleum ether at room temperature[47].

Quadrivalent manganese gives two series of complex fluorides — A_2MnF_6[50–52] and $AMnF_5$[50,52] (where A = Li, Na, K, Rb, Cs) — of which the brick-red compounds of the type $AMnF_5$ are the more reactive. These complex fluorides are obtained by fluorinating salts of the type $AMn^{2+}F_3$[52] or a mixture of the simple salts[48], e.g.

$$LiF+MnF_2 \xrightarrow[350°]{F_2} LiMnF_5.$$

Potassium pentafluoromanganate can be prepared by the action of bromine trifluoride on potassium permanganate with subsequent removal of excess bromine trifluoride under vacuum at 20°.[50] It is formed also by the reaction[50]

$$4KMnO_4+10SeF_4=4KMnF_5+10SeOF_2+3O_2.$$

Pentafluoromanganates are hydrolysed by water, and form brownish-black precipitates with dilute alkalis; in air they gradually decompose. Hydrogen reduces them at 250–275°: lithium pentafluoromanganate is reduced even at 150–200°, whereas the caesium salt is incompletely reduced[52].

Technetium and rhenium give the reactive fluorine compounds technetium hexafluoride[57], rhenium hexafluoride[54,55], and rhenium heptafluoride[56,57]. The volatile hexafluorides of technetium and rhenium are formed by reaction of the metal powders with fluorine (at 400° and 420° respectively), rhenium hexafluoride being obtained also by treating powdered rhenium with chlorine trifluoride at 300°.[55] On further treatment with fluorine, 1 mole of rhenium hexafluoride absorbs a further 0.5 mole of fluorine, to give the less volatile heptafluoride[56], which is probably thermally stable[57]. The infrared spectra of technetium and rhenium hexafluorides have been recorded, and the principal thermodynamic constants obtained[53,57]. All three higher fluorides are sensitive to moisture, but can be stored in a dry Pyrex glass vessel at room temperature for a long time[53,57]. Hydrolysis of technetium hexafluoride in the presence of sodium hydroxide gives a black precipitate, which dissolves on the addition of hydrogen peroxide[53]. Its behaviour is analogous to that of rhenium hexafluoride, which disproportionates on hydrolysis, giving insoluble rhenium dioxide, rhenic acid $HReO_4^-$, and hydrogen fluoride[54].

Rhenium hexafluoride is a vigorous oxidising agent, being reduced to the tetrafluoride by hydrogen at 200°, sulphur dioxide at 400°, and carbon monoxide at 300°.[54] With alkali metals it forms complexes of the type A_2ReF_8, which are readily hydrolysed by water[58].

6. Simple and Complex Fluorides of the Iron Subgroup

Since a group of five *d*-electrons is especially stable, iron(III) fluoride does not exhibit oxidising properties[59], and dissociates only at 1000° and 15 mm in a stream of nitrogen, being converted into iron(II) fluoride[60]. Cobalt, like iron, forms both a difluoride and a trifluoride, but, in contrast to iron(III) fluoride, cobalt(III) fluoride is a strong oxidising agent.

Cobalt trifluoride can be obtained by the action of fluorine on cobalt(II) fluoride or chloride at 150°.[61] It is a pale brown powder, whose physical properties and structure have been studied in detail[61]. It dissociates appreciably into cobalt(II) fluoride and fluorine in a stream of carbon dioxide at 250°–300°, and is completely dissociated at 350°. Reaction of cobalt trifluoride with water, aqueous acids, and aqueous alkalis is accompanied by very vigorous evolution of oxygen[61]. Cobalt trifluoride is widely used for the fluorination of organic compounds with the aim of preparing perfluorinated hydrocarbons. Its use for the fluorination of hydrocarbons containing about 1–20 carbon atoms has been described.

Compounds of higher molecular weight can also be fluorinated, although very considerable difficulties are involved. The fluorination of compounds containing oxygen[62] and nitrogen[63–66] has been described, but the yields are relatively low. Fluorination with cobalt trifluoride can be effected over the range 150–400° both in the vapour phase and in inert liquid perfluorinated solvents. The manufacture of perfluorinated oils for the gas-diffusion enrichment of uranium by means of cobalt trifluoride was suggested in the USA in 1941, although the cost of manufacture was extremely high. Fluorination with cobalt trifluoride has been described in detail[67,68].

The complex K_3CoF_6 was first obtained by the anodic oxidation of cobalt(II) fluoride dissolved in hydrofluoric acid, with subsequent treatment of the resulting $CoF_3.3\frac{1}{2}H_2O$ with solid potassium fluoride at -10°.[69] The corresponding ammonium complex cannot be obtained by this method[70].

Klemm and his coworkers suggested several dry methods. The first was based on the fluorination of mixtures of cobalt(II) chloride and salts containing the cation present in the final product[71], e.g.

$$3KCl+CoCl_2 \xrightarrow{F_2} K_3CoF_6.$$

The second method consists in fluorinating with dilute fluorine a complex salt containing no fluorine; for example, K_3CoF_6 can be obtained from $K_3Co(CN)_6$.[72,73] Hoppe and Klemm have reported the use of this method to prepare complexes A_3CoF_6, where A = Li, Na, K, Rb, Cs,[72,73] Ag,[74] Ba.[75] An attempt to obtain $LaCoF_6$ by fluorinating $LaCo(CN)_6$ was unsuccessful[75].

The pure A_3CoF_6 compounds possess strong oxidising properties, being decomposed by water with the separation of a black deposit and the evolution of oxygen. With aqueous perchloric acid they evolve a gas and form a bivalent cobalt salt. These complexes oxidise hydrochloric acid and acidified potassium iodide solution[74].

The previously described[71] compound K_3CoF_7 proved[72] to have the formula K_3CoF_6. At the present time only one complex of quadrivalent cobalt is known: when Cs_2CoCl_4[72] or $Cs_2Co(SO_4)_2.6H_2O$ is fluorinated, a brownish-yellow complex Cs_2CoF_6 is obtained[72,74]. The quadrivalent cobalt compound is less stable than Cs_3CoF_6.[74] Reactions of tervalent and quadrivalent cobalt complexes with organic compounds have not been studied. The physical properties of the complexes have been described[72–76].

The higher fluorides of nickel NiF_3 and NiF_4 have not yet been described, but their complex compounds of the types A_3NiF_6 and A_2NiF_6 are known.

Higher fluorides of nickel are interesting in view of their possible occurrence in electrochemical fluorination. The electrochemical fluorination of organic compounds containing oxygen, nitrogen, or sulphur is effected by passing a direct current through their solutions in anhydrous hydrogen fluoride. When nickel electrodes are used, a voltage of ~5 V is applied to the electrolytic cell, and fluorination is accompanied by relatively little cleavage of carbon–carbon bonds. Electrochemical fluorination is undoubtedly an anodic process. It has been suggested that the higher complex fluorides of nickel are active fluorine carriers[77]. This view finds indirect confirmation in the chemistry of quadrivalent nickel complexes.

The violet complex K_3NiF_6 is formed by the fluorination of a 1 : 3 mixture of potassium chloride with nickel sulphate[78] or nickel chloride[71] in a mixture of fluorine and carbon dioxide at 320°. The corresponding sodium complex is obtained similarly (from sodium chloride or bromate and nickel sulphate). Fluorination of a mixture of ACl (where A = K, Rb, Cs) and $NiCl_2$ occurs still more readily, even at 275°, diamagnetic red complexes A_2NiF_6 being obtained[71,79].

The complex K_2NiF_6 reacts very violently with water, a gas being evolved whose odour recalls that of ozone (OF_2 ?). It is relatively stable in dry air, and does not react when heated with hydrocarbons, aniline, dimethylaniline, or acetic anhydride, but reacts vigorously with acidic substances such as acetic and decanoic acids, phenol, and sulphuric and hydrochloric acids, being converted into greyish-green nickel(II) chloride:.

$$2A{-}H + K_2NiF_6 \rightarrow [H_2NiF_6] + 2KA \rightarrow NiF_2 + 2HF + 2F.$$

It is possible that similar processes occur also in electrochemical fluorination:

1. $Ni + F^- \xrightarrow{-2e} NiF_2$,
2. $NiF_2 + 2F^- + 2NR_3^HH^+ \xrightarrow{-ne} (NR_3^H)_2NiF_6$,
3. $(NR_3^H)_2NiF_6 + nF^- \xrightarrow[-nH_2]{-ne} (NR_3^F)_2NiF_6$,
4. $(NR_3^F)_2NiF_6 + 2NR_3^HH^+ \rightarrow (NR_3^H)_2NiF_6 + NR_3^F + H^+$,
5. $(NR_3)_2NiF_6 \xrightarrow[\text{off}]{\text{current}} (NR_3)_2NiF_4 + F_2$,

   $(NR_3)_2NiF_4 + 2HF \rightleftarrows NiF_2 + 2(NR_3^H)^+F^-$.

Such a mechanism is supported by the fact that, in spite of repeated attempts, electrochemical fluorination can be accomplished only at nickel anodes, except with a considerably higher overpotential at Monel-metal anodes[80]. Still further evidence in support of this mechanism is provided by the diminished yields which one of us has observed, and the decrease in stability of electrochemical fluorination, when anodes of low-grade nickel are used[81].

7. Higher Fluorides of the Platinum Metals

Among the light platinum metals, hexafluorides have been obtained of ruthenium and rhodium. Powdered ruthenium and rhodium explode in fluorine[82,83]. Ruthenium hexafluoride is a dark brown solid melting at 54°.[82] It is less volatile than the corresponding molybdenum and technetium compounds. It reacts rapidly with Pyrex glass, and to a less extent with quartz. Ruthenium hexafluoride can be stored in a nickel vessel without decomposition for a long time[82].

Rhodium hexafluoride is a black substance (the vapour being reddish-brown), resembling ruthenium hexafluoride. It breaks down into fluorine and a lower fluoride even at room temperature[83]:

$$RhF_6 \rightarrow RhF_5 + \frac{1}{2}F_2.$$

Both ruthenium and rhodium hexafluorides are extremely reactive substances: they form complexes with xenon[84,85] analogous to $XePtF_6$.[86] The infrared spectra of these hexafluorides have been recorded, and their structure has been studied[82,83].

Ruthenium pentafluoride is formed from the elements at 300°[87] and when ruthenium dioxide is treated with fluorine or with bromine pentafluoride[88]. The dark green compound[87,89] fumes strongly in the air, and reacts violently with water, being converted into a black lower oxide of ruthenium[87]. Ruthenium pentafluoride is a vigorous oxidising and fluorinating agent, iodine being oxidised to iodine pentafluoride at 160°, and sulphur to sulphur hexafluoride at 0°. At high temperatures it converts copper and silver into fluorides, and oxidises hydrogen chloride to chlorine, but it reacts only slightly with dry benzene and toluene. The reactive complexes $ARuF_6$ evolve oxygen on interaction with water[87].

Ruthenium tetrafluoride has been obtained by reducing the pentafluoride with iodine in iodine pentafluoride solution[90]. It is a non-volatile yellow solid, which blackens in moist air, and reacts violently with water, being converted into ruthenium dioxide.

Rhodium tetrafluoride is obtained by the action of fluorine on rhodium, its trichloride, or its trifluoride at 500° or by dissolving rhodium tribromide in bromine trifluoride and then evaporating off the latter. It is a hygroscopic powder, which oxidises hydrochloric acid to chlorine; it does not react with ether or carbon tetrachloride at room temperature[91]. Complexes A_2RhF_6, which are sensitive to moisture, being violently decomposed by water with the evolution of gases, have been prepared[91].

Palladium trifluoride is obtained by the action of fluorine on the dichloride[92], the di-iodide[93], or palladium[94], or by decomposing $PdF_3.BrF_3$ in a vacuum at 200°.[92] It is a hygroscopic black powder, which evolves oxygen on contact with cold water, oxidises hydrogen chloride to chlorine, and reacts vigorously when heated with iodine, sulphur, phosphorus, carbon, sodium, magnesium, aluminium, or iron[88]. Complex fluorides of quadrivalent palladium A_2PdF_6 are known. The complexes are sensitive to moisture, decompose rapidly, and blacken in moist air[92,95].

A diminution in the stability of the higher valencies with increasing number of *d*-electrons is very characteristic of Group VIII in the Periodic System. This applies to all properties. Thus, in the iron family, iron trifluoride does not exhibit oxidising properties, cobalt trifluoride is an extremely strong oxidising agent, and nickel trifluoride (and tetrafluoride) have not been prepared, but from the properties of their complexes, appear to be extraordinarily strong oxidants. A similar increase in oxidising power from left to right is characteristic also of the higher fluorides of the platinum metals.

More than fifty years ago Ruff and his coworkers described the preparation, identification, and properties of three fluorides — OsF_4, OsF_6, and OsF_8 — of osmium[96]. But when the reaction of elementary fluorine with heated

osmium was reinvestigated, a single volatile reaction product was obtained, and was identified as osmium hexafluoride[97]. This compound is hydrolysed by aqueous alkali with the evolution of heat and a gas smelling like ozone, and it oxidises water to oxygen[24,97]. Osmium hexafluoride is reduced by a deficiency of iodine in iodine pentafluoride solution[98]. The reaction begins at room temperature, and terminates at 50° according to the equation

$$10OsF_6+I_2 \rightarrow 10OsF_5+2IF_5.$$

The yield is quantitative. Osmium hexafluoride undergoes a similar transformation under the influence of ultraviolet radiation[98].

Golden-yellow iridium hexafluoride is obtained by the action of fluorine on iridium at 260°; it melts at 44.4° and boils at 53°.[99] Iridium hexafluoride is an extremely strong oxidising agent, reacting with hydrogen, sulphur, phosphorus, and halogens. It fluorinates even chlorine. It attacks glass even at room temperature, and fluorinates many metals, including platinum. Iridium hexafluoride oxidises water with the evolution of a gas smelling of ozone[24,99], and is reduced by carbon tetrachloride and by petroleum ether even in the cold. It is relatively stable in quartz, and does not decompose in the latter even at 400°.[99] The extraordinary reactivity of iridium hexafluoride is indicated also by its ability to fluorinate silver chloride. Polytetrafluoroethylene evolves carbon tetrafluoride on interaction with iridium hexafluoride[100].

In contrast to osmium, iridium forms complex fluorides of the type $AIrF_6$, which are strong oxidising agents. Hexafluoroiridates evolve oxygen on reaction with water, and are rapidly decomposed by moist air[99]. The extremely strong oxidant $IrOF_4$ is decomposed by water with the evolution of oxygen[99].

Platinum tetrafluoride decomposes with the evolution of fluorine when strongly heated[101]. The hexafluoride has recently been obtained[102,103] by the combustion of platinum in fluorine under the influence of an electric spark discharge; it is probably the strongest of all known fluorinating agents[24,26,103]. When stored in glass platinum hexafluoride, like neptunium and plutonium hexafluorides, undergoes photochemical decomposition[24]. It is unstable, undergoing rapid and complete decomposition at 280°.[24] It converts solid products of the radiolysis of neptunium and plutonium hexafluorides into the hexafluorides, although the yield is not high[24,103].

Platinum hexafluoride readily fluorinates bromine trifluoride to the pentafluoride at room temperature[103], reacts violently with metallic uranium to form the hexafluoride, and decomposes water with the evolution of oxygen[24]. The brownish-red platinum hexafluoride vapour oxidises molecular oxygen to a complex of the unusual type $O_2^+PtF_6^-$.[104] Since the first ionisation potential of oxygen $O_2 \rightarrow O_2^+$ is 12.2 eV, which is higher than that of xenon (12.13 eV), it was suggested that formation of xenon hexafluoroplatinate

$$Xe+PtF_6 \rightarrow Xe^+PtF_6^-,$$

was possible. In fact, this method has been used to obtain the first chemical compound of xenon, which is orange in colour, is stable at 20°, and sublimes in a vacuum[86]. It is readily hydrolysed by water:

$$2XePtF_6+6H_2O \rightarrow 2Xe+O_2+2PtO_2+12HF.$$

8. Higher Fluorides of Copper, Silver, Gold, and Mercury

Copper forms a stable difluoride, which is devoid of oxidising power[105]. Copper trifluoride has not been described, although it may be involved as a fluorine carrier in the catalytic fluorination of organic compounds by elementary fluorine on copper gauze[106,107].

A complex K_3CuF_6 is formed[71] by the action of fluorine on a mixture of copper(II) and potassium chlorides at 250°. This substance is vigorously decomposed by water with the evolution of an unidentified gas (either O_2, O_3, or OF_2)[71]. Complexes A_3CuF_6 (A = Rb, Cs) are known[18]. Complexes of tervalent copper may be expected to exhibit interesting fluorinating properties.

Silver difluoride is one of the most thoroughly studied and widely used fluorinating agents. Treatment of silver or its salts with fluorine at 150–250° yields the black modification of the difluoride. The yellow modification can be obtained by fluorinating silver with chlorine trifluoride. The properties of silver difluoride have been studied in some detail[108].

Silver difluoride is widely used for the fluorination of organic compounds, being a more powerful fluorinating agent than is cobalt trifluoride[109]. It fluorinates carbon monoxide to carbonyl fluoride[110], and converts hydrocarbons and halogenated derivatives into perfluorohydrocarbons. Silver difluoride has the advantage over cobalt trifluoride in fluorinating chloro-derivatives, but, because of the poorer free-flowing properties of the powder and its more corrosive nature, it is inferior to the latter in the vapour-phase fluorination of hydrocarbons[111]. It has been reported that organic disulphides are selectively fluorinated by silver difluoride to derivatives of sulphur tetrafluoride, great prospects thus being opened up in the synthesis of organofluorine compounds. A special investigation has shown that silver difluoride is irreplaceable for this purpose[112]. This compound probably plays an extremely favourable role in the catalytic fluorination of organic compounds on a silvered wire[113].

Complex compounds based on the unknown silver trifluoride have been described[114-117]. Compounds of the type $AAgF_4$ (A = K, Cs) and $BaAgF_5$ react violently with water; at 200° $BaAgF_5$ is converted into the more stable compound $BaAgF_4$, fluorine being eliminated[117]. X-Ray examination has shown that compounds which had been regarded as $CsAgF_6$ and $CsAuF_6$ did not in fact have this structure[117].

Gold trifluoride has been obtained, by fluorinating gold with fluorine or with bromine trifluoride, as an orange powder, which decomposes at 500°. It is a strong fluorinating agent, reacting violently with water. It ignites organic compounds even at room temperature, and reacts smoothly with carbon tetrachloride at 40°.[114,118] Gold trifluoride probably has a favourable influence on the catalytic fluorination of organic compounds on a gold-plated copper wire[119].

A series of complex fluorides of the type $AAuF_4$ (A = Na, K, Cs, Ag) has been obtained by fluorinating the chloroaurates with elementary fluorine or by the reaction of gold trifluoride in bromine trifluoride with the metal fluorides. The complex $AgAuF_4$ does not react with carbon tetrachloride, but it is reduced by benzene, and reacts violently with cold water[114,118].

Mercuric fluoride has long been used as a reagent. It is a hygroscopic white substance of melting point 645°, which immediately becomes yellow in the air[120]. Its preparation has been described[120-122]. Mercury difluoride is used for the replacement of other halogens by fluorine, but at temperatures above 100° it mildly fluorinates hydrocarbons[120,123]. An interesting property is its ability to add on to fluorinated compounds containing multiple bonds (azomethines[124], alkenes[125,126]), so that it can be used for synthetic purposes according to the scheme[124]

$$CF_3N{=}CF_2 + HgF_2 \rightarrow (CF_3)_2NHgN(CF_3)_2 \xrightarrow{Br_2} (CF_3)_2NBr \xrightarrow{CF_2{=}CF_2} (CF_3)_2NCF_2CF_2Br.$$

III. HIGHER FLUORIDES OF ELEMENTS IN THE MAIN SUBGROUPS OF THE PERIODIC SYSTEM

In the following subgroups a high oxidising power is exhibited by the fluorides of tervalent thallium, quadrivalent lead, quinquevalent antimony and bismuth, oxygen, and sexivalent polonium, as well as all halogen fluorides. The fluorides of the inert gases which have recently been described must probably be included among fluorides of high oxidising power.

1. Higher Fluorides of Thallium, Lead, Antimony, and Bismuth

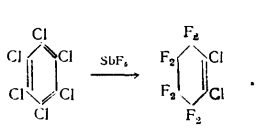
Thallium trifluoride can be obtained in several ways — by treating the oxide with fluorine at 300°,[127] or with bromine trifluoride[122] or sulphur tetrafluoride[121], by the action of chlorine trifluoride on metallic thallium[127], and by the interaction of thallium iodate with bromine trifluoride[122] — and is a white solid which darkens in moist air, being instantaneously hydrolysed by water with the formation of a black precipitate of the hydroxide

$$TlF_3 + 3H_2O \rightarrow Tl(OH)_3 + 3HF,$$

this giving the oxide Tl_2O_3 on being heated[122]. Thallium trifluoride does not react with liquid ammonia, but paraffin, benzene, and chloroform do interact with it, fluorination perhaps occurring here[127].

Lead tetrafluoride is obtained by fluorinating the difluoride with fluorine at 300°.[128] It consists of colourless crystals, which darken in the air owing to hydrolysis, and melt at around 600°.[128] Lead tetrafluoride vigorously fluorinates hydrocarbons in both liquid and vapour phases[129-131]. In practice, however, it is very difficult to use, since a eutectic mixture, containing about 60% PbF_2 + 40% PbF_4, attacks the reaction vessel[131]. The use has been reported of a mixture of lead dioxide, lead tetra-acetate, and anhydrous hydrogen fluoride[132] or of lead dioxide and sulphur tetrafluoride[133] in an autoclave, for adding fluorine at the double bond of halogenated alkenes.

Fluorides of tervalent and quinquevalent antimony are widely used in the exchange of other halogens for fluorine (the Swarts reaction)[134]. However, antimony pentafluoride is capable not only of exchanging chlorine for fluorine but also of adding fluorine to the double bond in chlorinated aromatic and unsaturated compounds[135,136]:



Antimony pentafluoride can be obtained from the pentachloride and anhydrous hydrogen fluoride or from the trifluoride and fluorine. It forms a hydrate $SbF_5.2H_2O$, as well as complexes which are stable in aqueous solution[137].

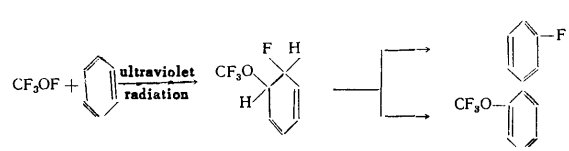
Bismuth pentafluoride is a stronger oxidising agent than is antimony pentafluoride. It reacts vigorously with water, a gas smelling of ozone being evolved[138,139], and reacts readily with paraffin oil, which is not blackened[139]. Its successful use for the synthesis of perfluorohydrocarbons has been reported[140]. However, the practical application of bismuth pentafluoride is made difficult by the complexity of its preparation, which involves passing fluorine over bismuth trifluoride at 450–500°. At this temperature the pentafluoride sublimes into the cooled part of the reaction vessel as long white needles, which instantly become yellow on contact with the air[138,139]. The yield of bismuth pentafluoride is low, obviously owing to its decomposition in the gaseous state[138]. Bismuth pentafluoride converts uranium tetrafluoride and oxide into uranium hexafluoride, and bromine into bromine trifluoride, which itself is converted into bromine pentafluoride[139].

The complex hexafluorobismuthates $ABiF_6$ are hygroscopic, and are decomposed even by 40% hydrofluoric acid[138]. Bismuth pentoxide reacts with the 40% acid with the evolution of a gas smelling of ozone. The resulting solution possesses extremely strong oxidising properties[138].

2. Fluorides of the Oxygen Subgroup

Oxygen forms with fluorine the difluoride OF_2 and several fluorides — O_2F_2, O_3F_2, and O_4F_2 — which are richer in oxygen[141]. Compounds of fluorine and oxygen with other elements are also known, such as trifluoromethyl hypofluorite CF_3OF,[141,142] fluorine nitrate NO_3F, fluorine perchlorate $ClFO_4$,[141] and compounds of the type XO_3F, where X = Cl, Br, I.[143] The oxygen fluorides are extremely strong oxidising agents even at low temperatures, and are employed in rocket technology[144-146]. Until recently oxygen difluoride has not been used for the synthesis of organofluorine compounds. When it interacts with benzene[147] and primary aliphatic amines[148], oxygen-containing products (quinones[147] and nitroso-compounds[148]) are isolated. Reaction with alkenes and alkynes yields α-fluoro-ketones, fluorohydrins, and $\alpha\alpha$-difluoro-ketones[149].

The readily available trifluoromethyl hypofluorite[141,142] adds quantitatively to the double bonds of alkenes[150-152]. It reacts slowly with benzene according to the equation[152]



Under the influence of ultraviolet radiation the hypofluorite reacts with methane[152]:

$$CF_3OF + CH_4 \xrightarrow[\text{radiation}]{\text{ultraviolet}} COF_2 + CH_3F + HF.$$

Among this group the most suitable for use for the preparation of organofluorine compounds is fluorine chlorate, which can be prepared by the action of fluorine on cooled potassium chlorate[153], by heating perchlorates or perchloric acid with excess of fluorosulphuric acid at a high temperature[154], or by treating them with a mixture of this acid and antimony pentafluoride at room temperature[155]. Fluorine

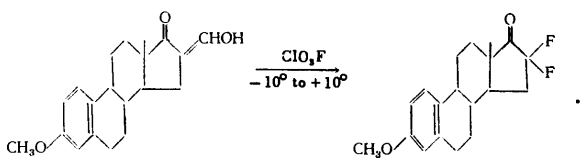
chlorate is a colourless substance melting at -110° and boiling at -46°.[153]. When heated it decomposes[156]:

$$2ClFO_3 = 2ClF + 3O_2.$$

Fluorine chlorate is able to replace the hydrogen atoms in reactive methylene groups[157,158], e.g. [157]

$$p\text{-}BrC_6H_4COCH_2COC_6H_4\text{—}Br\text{-}p \xrightarrow[\text{pyridine}]{ClO_3F,\ -10^\circ \text{ to } +10^\circ} p\text{-}BrC_6H_4COCF_2COC_6H_4\text{—}Br\text{-}p.$$

When this reagent is passed into an alcoholic solution of the sodium derivative of diethyl malonate, diethyl difluoromalonate is obtained[158]. Fluorine chlorate is employed for the fluorination of steroids[159-161], e.g. [161]



A method has recently been proposed for preparing *o*- and *p*-fluorophenols by treating the phenols with fluorine chlorate[162].

Sulphur tetrafluoride is used at the present time for replacing oxygen-containing groups by fluorine[163]. The hexafluoride is extremely stable[164]. The hexafluorides of selenium and tellurium do not exhibit oxidising properties[164].

It was earlier predicted that polonium would form a compound analogous to the Group VI hexafluorides SF_6, SeF_6, MoF_6, WF_6, and UF_6. However, no volatile compound was obtained when polonium-210 was heated in fluorine or when it was treated with liquid bromine trifluoride[26,165,166]. Treatment of polonium-208 with fluorine gave a volatile polonium fluoride, which underwent subsequent breakdown (chemical or radioactive). Perhaps its reactivity explains the lack of success of earlier attempts to prepare a volatile polonium compound[167].

3. Simple and Complex Halogen Fluorides

The halogen fluorides are extremely reactive substances, which can be arranged in the seq' ence of diminishing reactivity

$$F_2 > ClF_3 > BrF_5 > IF_7 > FCl > ,rF_3 > IF_5 > BrF^{168}.$$

Their reactions with many organic substances are very vigorous and may become explosive in character, so that the success of an experiment depends on the appropriate choice of technique.

Chlorine trifluoride, bromine trifluoride, and iodine pentafluoride are the most important as fluorinating agents, and possess several great advantages over both elementary fluorine and higher fluorides of metals. Firstly, they are liquid over quite a wide range of temperatures close to the normal, so that they can be more easily stored and used than can fluorine. Secondly, they do not leave any solid residues of the type of cobalt difluoride or silver fluoride after use, so that they are equally suitable for vapour-phase and for liquid-phase processes. Hitherto, however, the use of halogen fluorides has not been very widespread. The reasons are that they are too reactive and also that they usually introduce into the molecule not only fluorine but also, depending on the fluoride used, chlorine, bromine, or even iodine[169]. Sometimes this property is specially utilised; thus a mixture of halogens and halogen fluorides is an efficient source of halogen monofluorides in reactions with alkenes[170-172]:

$$IF_5 + 2I_2 = 5IF,$$

$$\overset{\delta+}{C}F_2{=}\overset{\delta-}{C}F\text{—}CF_3 + \overset{\delta+}{I}\,\overset{\delta-}{F} \rightarrow CF_3CFICF_3.$$

Iodine pentafluoride reacts with most organic compounds quite violently, sometimes even with ignition and evolution of hydrogen fluoride. However, insufficient study has been made either of the products or of the conditions of the reaction. Nevertheless, it is known that fluorobenzene is formed by reaction with benzene in the presence of the fluorides of arsenic and antimony[173].

The interaction of carbon tetrahalides with iodine pentafluoride has been described in detail[174], and the fluorination of carbon disulphide and carbonyl chloride with iodine pentafluoride has been studied[174]. Emeleus and Haszeldine obtained pentafluoroiodoethane from tetraiodoethylene and this pentafluoride[174].

Iodine heptafluoride is considerably more reactive than the pentafluoride. Although little work has been done on its reactions with organic substances, it is known to react with benzene in the presence of arsenic and antimony fluorides, yielding fluorobenzene[173].

Bromine trifluoride reacts explosively with the usual organic compounds. It can be successfully used for the partial replacement of other halogens by fluorine in polyhalogenated compounds, and for addition to multiple bonds in hexachlorobenzene, hexabromobenzene, and pentachlorotrifluoromethylbenzene[175,176]. However, this involves the addition to the double bonds not only of fluorine but also to some extent of bromine, obviously because the highly reactive bromine monofluoride is formed as an intermediate product. Bromine trifluoride can probably be used also for the fluorination of compounds containing some hydrogen; at least in the presence of boron trifluoride it replaces hydrogen in nitrobenzene by fluorine[173]. Selective fluorination of the nitrile group and the keto-group by bromine trifluoride in the presence of hydrogen fluoride or iodine pentafluoride at -15° has been reported[177,178]. Thus acetonitrile is converted into 1,1,1-trifluoroethane in yields of 70–90%. Under the same conditions acetone is converted into 2,2-difluoropropane in good yield (90%), but ketones of more complicated structure undergo cleavage.

Few data are available on the reactions of bromine pentafluoride. In the presence of phosphorus pentafluoride at low temperatures, for example, it converts bromobenzene into *p*-bromofluorobenzene[173].

Chlorine monofluoride is a very reactive gas, which sets fire to organic compounds. However, it can act on highly halogenated hydrocarbons, saturating double bonds and replacing hydrogen and part of the chlorine by fluorine[179].

Technical chlorine trifluoride is widely used in atomic and rocket technology[180]. In the absence of appropriate precautions, the interaction of this compound with the usual organic compounds is accompanied by explosion.

The reaction of benzene with chlorine trifluoride in polyfluorinated solvents[173] or carbon tetrachloride[181,182] in the presence of salts of various elements or of halogens as catalysts leads at low temperatures to the formation of fluoro- and chloro-benzenes[181,182], accompanied by low

yields of products involving addition of halogens to the ring carbon atoms[181,182]. Under the same conditions chlorobenzene gives *ortho*- and *para*-substitution products. Liquid-phase fluorination probably has an electrophilic mechanism[181,183]:

$$ClF_3+2CoF_2 \rightarrow 2CoF_3+ClF,$$
$$ClF_3+CoF_3 \rightarrow F^+ + CoF_4^- + ClF.$$

The vapour-phase halogenation of benzene with chlorine trifluoride, which is a free-radical process, yields a complex mixture of chlorofluorocyclohexanes[183,184]:

$$ClF_3 \rightarrow ClF+2F^{\cdot},$$
$$ClF \rightarrow Cl^{\cdot}+F^{\cdot},$$
$$C_6H_6 \xrightarrow{Cl^{\cdot},F^{\cdot}} C_6H_xCl_yF_z\ (x+y+z)=12.$$

Besides highly halogenated cyclohexanes, the mixture also contains chloro- and chlorofluoro-benzenes.

The liquid-phase halogenation of hexachlorobenzene with excess of chlorine trifluoride involves a chain of additions and vinyl and allyl substitutions leading to the formation of chlorofluorocyclohexenes $C_6F_nCl_{10-n}$ (n = 4–6). A very large excess (400%) yields chlorofluorocyclohexanes $C_6F_nCl_{12-n}$ (n = 5–7)[185].

Most of the information on the reactions of chlorine trifluoride with organic substances will be found in the patent literature, the investigations being aimed at obtaining greases and oils. Without going into details, we can summarise the results by stating that highly fluorinated chlorofluorohydrocarbons can be obtained by selecting appropriate conditions, but that, because of steric hindrance due to the massive chlorine atoms, replacement of the hydrogen is not complete[183,184], so that the products of the chlorofluorination are less stable, both thermally and chemically, than oils obtained in other ways.

A higher degree of replacement of hydrogen, and at the same time of chlorine, can be obtained in the presence of antimony salts, which obviously promote substitution of chlorine by fluorine, and thereby diminish the steric hindrance to replacement of the remaining hydrogen atoms[186]. More stable products are obtained by treating perchlorinated unsaturated and aromatic compounds[175,176,185,187].

The fluorination of carbon or coal, both by fluorine itself and by halogen fluorides, is of intrinsic interest. When fluorine, a mixture of fluorine and chlorine, or chlorine trifluoride is passed, diluted with nitrogen, through graphite or wood charcoal at temperatures between 160° and 660°, various perfluoro- or polychlorofluoro-carbons containing one or more carbon atoms are formed. Similar results are obtained with other halogen fluorides. The use of coal makes it possible to obtain products of far higher molecular weight and oils which distil between 100° at 1 atm and 250° at 20 mm.[188]

All halogen fluorides form complexes with metal fluorides. Such complexes can be obtained by two main methods — (1) direct mixing of the initial components[189,190], e.g.

$$AF + BrF_3 \rightarrow ABrF_4;$$

or (2) fluorination of metal halides with fluorine at high temperatures[191–195]

$$ABr \xrightarrow[t^\circ]{F_2} ABrF_4.$$

Complex halogen fluorides can also be prepared by treating iodates[122], chlorates[196], and metals (gold)[114] with bromine trifluoride. Iodine pentafluoride and the complex KIF_6 are obtained by the action of sulphur tetrafluoride on potassium iodate[197].

At the present time the following compounds are known

$$ACIF_4\ (A=K, Rb, Cs, Ag);\ RbClF_6,$$
$$ABrF_4\left(A=K, Rb, Cs, \frac{Ba}{2}\right);\ RbBrF_6;$$
$$AIF_4\ (A=K, Rb, Cs);\ AIF_6\ (A=Rb, Cs).$$

These complexes react violently with water, evolving oxygen, liberate iodine from potassium iodide solution[189,191,193,198], and oxidise nickel(II) salts to the quadrivalent state[191,193,198]. All the complexes obtained are milder halogenating agents than the corresponding halogen fluorides. The reactivity of the complex depends on the nature of the cation present in the outer sphere. Thus whereas under normal conditions $KBrF_4$ does not react with acetone, dioxan, or carbon tetrachloride, $AgBrF_4$ and $BaBr_2F_8$ ignite ether, acetone, petrol, and dioxan, but do not react with carbon tetrachloride. Bromine trifluoride not only ignites acetone and dioxan but also reacts violently with carbon tetrachloride[189]. The thermal stability of the complex halogen fluorides is increased by replacing the potassium cation by rubidium, and especially by caesium, while the violence of the reaction with water increases from iodine derivatives to those of bromine and chlorine[194].

The infrared spectra of the complex halogen fluorides have been recorded[194], their magnetic susceptibilities have been measured[194], and the structure of these interesting compounds has been discussed[199]. The fact that they exhibit a wide range of fluorinating activity makes them extremely promising materials for the synthesis of various organofluorine compounds.

In the electrochemical fluorination of salts of various amines it has been noted that bromide and iodide (but not chloride) anions have a favourable effect on the yield of perfluorinated products. The presence of iodine can be readily detected in fluorinated iodides from the characteristic colour, both in the electrolyte and in the perfluorinated raw material. The favourable effect of bromine and iodine may perhaps be explained by the mild fluorinating action of the complexes formed by organic bases with halogen fluorides.

4. Fluorine Compounds of the Inert Gases

As early as 1933 Pauling predicted the existence of KrF_6, XeF_6, and XeF_8. The first such compound, xenon hexafluoroplatinate, was obtained by oxidising xenon with platinum hexafluoride[86]. Four fluorides of xenon — XeF_2, XeF_4, XeF_6, and XeF_8 — have now been prepared[200,201].

Xenon difluoride is a colourless substance, which forms crystals reaching several millimetres in size. It melts at 140°, and can be supercooled to 50° without solidifying[201]. It is stable at room temperature, and can be stored in nickel or quartz vessels for several months. Xenon difluoride can be kept for a long time in sealed glass tubes at the temperature of solid carbon dioxide, but at room temperature it is slowly decomposed, even in the dark, by interacting with the glass. It reacts vigorously with methanol, and slowly with water. In solutions of alkalis and dilute acids it is decomposed, not especially violently, and it liberates iodine from acidified [potassium iodide] solution; it decomposes in dry paraffin[201], and dissolves in anhydrous hydrogen fluoride without decomposition. At

400° it is completely reduced by hydrogen to xenon and hydrogen fluoride[201].

Xenon tetrafluoride exists as colourless crystals melting at 114°.[201] It readily sublimes in a vacuum as large colourless crystals. Xenon tetrafluoride remains unchanged under vacuum in nickel or Pyrex glass for a month[200,201]. It attacks glass with the formation of silicon tetrafluoride and oxygen. Its mixtures with sugar or sulphur explode similarly to those with potassium chlorate. When deposited on paper or cotton wool, dry xenon tetrafluoride explodes on being heated; after it has become moist in the air, it instantly chars paper, and frequently it may even ignite spontaneously[201].

Xenon tetrafluoride fumes in the air, being hydrolysed to $Xe(OH)_4$, and dissolves in water, glacial acetic acid, and concentrated nitric and sulphuric acids; it reacts with acetic acid or acetic anhydride to give a crystalline substance, possibly xenon acetate. Cyclopentadiene, tetrahydrofuran, dioxan, and ethanol ignite under the influence of xenon tetrafluoride. Petrol dissolves it, and acetone reacts with it. Xenon tetrafluoride neither dissolves in nor reacts with carbon disulphide, carbon tetrachloride, dimethylformamide, diethyl ether, cyclohexane, and perfluoroheptane[201]. It oxidises metallic platinum to the tetrafluoride[201].

Xenon hexafluoride is a colourless crystalline substance of melting point 47.7° ± 0.2°;[201] it is stable at room temperature, and can be kept in a nickel vessel without decomposition for a week. Samples which have been sealed in quartz react slowly with the latter to give a colourless transparent liquid[202]. It dissolves in anhydrous hydrogen fluoride[202], the resulting solutions, unlike those of the difluoride and the tetrafluoride, possessing a high electrical conductivity, perhaps as a result of dissociation into the ions XeF_5^+ and HF_2^-. Hydrogen at room temperature and mercury at 100° reduce xenon hexafluoride to elementary xenon[201].

Xenon tetrafluoride and hexafluoride are hydrolysed according to the equations[203]

$$XeF_2 + H_2O \rightarrow Xe + 0.5\,O_2 + 2\,HF,$$
$$3XeF_4 + 6\,H_2O \rightarrow XeO_3 + 2Xe + 1.5\,O_2 + 12\,HF,$$
$$XeF_6 + 3\,H_2O \rightarrow XeO_3 + 6\,HF.$$

Alkaline hydrolysis of xenon hexafluoride yields xenic acid[201]. With boron trifluoride and arsenic pentafluoride at room temperature xenon hexafluoride forms addition products[201].

Xenon octafluoride has recently been synthesised in a sealed tube at room temperature. It is an unstable pale yellow gas which, when cooled in liquid nitrogen, is converted into a yellow solid[201,204].

The fluorides of xenon are of interest for the selective fluorination of alkenes, which can be effected in the vapour phase at room temperature. The xenon which is formed can be easily separated from the reaction product[205]. The reactivity of the fluorides increases with the proportion of fluorine in the molecule. Thus xenon hexafluoride, the most reactive of those studied, causes cleavage of the perfluoropropene molecule with the formation of hexafluoroethane and carbon tetrafluoride, whereas xenon difluoride does not react even after six days. The reaction with the tetrafluoride is represented by the equation

$$XeF_4 + 2\,CF_3CF{=}CF_2 \rightarrow 2\,CF_3CF_2CF_3 + Xe.$$

An interesting rearrangement takes place in the reaction of the xenon fluorides with aliphatic alkenes. Ethylene reacts with xenon difluoride and tetrafluoride at room temperature to form 1,1- and 1,2-difluoroethanes in 35% and 45% yield respectively. With propene, however, these fluorides give 1,1-difluoropropane as the main product (65%):

$$\left.\begin{matrix}XeF_2\\XeF_4\end{matrix}\right\} + \begin{matrix}CH_2{=}CH_2 \rightarrow CH_2FCH_2F + CH_3CHF_2 + Xe,\\CH_3CH{=}CH_2 \rightarrow CH_3CH_2CHF_2 + Xe.\end{matrix}$$

The relative instability of 1,2-difluoroethane and the enhanced stability of 1,1-difluoroethane suggest that the products formed initially isomerise under the reaction conditions into *gem*-difluorides. Furthermore, hydrogen fluoride is detected in the reaction mixture when the fluorides react with propene, which indicates partial fluorination of the methyl (allyl) group[205].

An unknown fluoride of radon RnF_x has been synthesised from the elements at 400°.[200,201] It is more stable and less volatile than xenon tetrafluoride. It is also reduced by hydrogen less vigorously than is the latter: at 200° the radon fluoride is stable in hydrogen, but at 500° and a hydrogen pressure of 800 mm it is completely reduced in 15 min.[200]

Krypton difluoride has now been obtained[206], by photochemical interaction of the elements mixed with argon[201] and by the action of a silent discharge on a mixture of the elements at low pressures (~20 mm) and temperatures (-183°)[206]. The difluoride is a crystalline substance which sublimes at temperatures considerably below 0°. It is kept in a dry Pyrex glass or polychlorotrifluoroethylene container at the temperature of solid carbon dioxide. It undergoes spontaneous decomposition at room temperature.

Hydrolysis of krypton difluoride is analogous to that of xenon difluoride[206]:

$$KrF_2 + H_2O \rightarrow Kr + 0.5\,O_2 + 2\,HF.$$

Hydrolysis is rapid also in acid solution, in contrast to xenon difluoride, which can exist in acid solution for a long time. Krypton difluoride reacts with antimony pentafluoride at -20° to form the compound $KrF_2.SbF_5$, this salt being more stable and less volatile than the difluoride itself. The complex is analogous to the salt $XeF_2.SbF_5$.[201,206]

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All fluorides of high oxidising power can be divided into five groups according to their oxidising activity. Assignment to one group or another is based on general chemical properties, and the boundaries between the groups are to some extent arbitrary.

I	II	III	IV	V
NiF_4, NiF_3 CoF_4 CuF_3 AgF_3 OsF_6 NdF_4 DyF_4 PdF_4	$ClF_3 > BrF_3 > IF_7 > ClF$ $PtF_6 > PuF_6$ RuF_6, $NpF_6 > BrF_5$ RhF_6, $IrF_6 > BrF_5$ $CrF_6 > MnF_4$ XeF_6 OsF_6	$AuF_3 > AgF_2 > CoF_3$ BiF_5 BrF_3 RuF_5 UF_6 $XeF_6 > XeF_4$ KrF_2	MnF_3 $PbF_4 > CeF_4$ PdF_3 RuF_4 RhF_4 IF_5 CrF_5 TlF_3 TbF_4 TcF_6 XeF_2 CF_3OF $FClO_3$	VF_5 SbF_5 HgF_2

The first group comprises higher fluorides which, because of their high reactivity and thermodynamic instability, have not yet been obtained in the free state, although they exist as complex derivatives. The second group includes fluorides possessing very high fluorinating power, being capable of fluorinating halides to halogen fluorides, and all other elements to higher fluorides; they ignite organic compounds even at room temperature. The third group contains fluorides which are capable of displacing chlorine from hydrochloric acid and oxygen (sometimes as ozone or oxygen difluoride) from water, and reacting with organic compounds to replace hydrogen by fluorine atoms; these fluorides may ignite on contact with some organic compounds at room temperature. The fourth group is represented by fluorides possessing moderate reactivity, although capable of replacing hydrogen by fluorine atoms. The fifth group comprises fluorides which, while being oxidising agents, are incapable of substituting fluorine for hydrogen in organic compounds, but are able in isolated cases to add fluorine to multiple bonds. In some cases the relative activities of the fluorides within the groups are known.

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OXIDATION OF ORGANIC COMPOUNDS WITH ACTIVE MANGANESE DIOXIDE

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I. INTRODUCTION

New oxidants, possessing a wide range of action and great selectivity, have been discovered in recent years, among them being nickel peroxide[1], manganese(III) acetate[2], osmium tetroxide, the chromium trioxide–pyridine complex[3], selenium dioxide[4], etc. An important place in this series is occupied by active manganese dioxide, which since 1948 has found wide application for the oxidation of various classes of substances, especially unstable natural

compounds containing a hydroxy-group. Manganese dioxide exists in several crystalline forms[5], some of them being encountered in minerals.

Since the discovery by Ball et al.[6] of the method of selectively oxidising the polyene alcohol vitamin A_1 with specially prepared manganese dioxide, this oxidant has attracted the attention of a large number of research workers. The selective action of active manganese dioxide and the mild reaction conditions make this reagent very convenient for the oxidation of labile polyene and polyenyne alcohols, steroids, and vitamins. Whereas manganese dioxide was presented in the earlier paper as a specific reagent for the oxidation of $\alpha\beta$-unsaturated hydroxy-compounds, subsequent investigations have considerably extended the limits to its possible application.

Hitherto the method of oxidation with manganese dioxide has been presented in isolated papers and incomplete reviews[7-11], covering by no means all the experimental results. The aim of the present review is to systematise the main investigations in this field, attention being paid to oxidation with active manganese dioxide in neutral medium.

II. TYPES OF MANGANESE DIOXIDE AND METHODS OF PREPARATION

Following Ball's discovery, quite contradictory information appeared in the literature on the oxidation of alcohols by manganese dioxide. Thus Ball[6] and Turner[12] were unable to oxidise benzyl alcohol, whereas Harfenist[13] and Highet[14] obtained benzaldehyde in excellent yields under the same conditions. It can readily be seen that the reason for such discrepancies in the results is the varying oxidising power of the numerous modifications of manganese dioxide. The type of the manganese dioxide is determined primarily by the mode of preparation. Unfortunately, it is difficult to obtain a dioxide of standard activity which might serve as a criterion for comparing the oxidising efficiency of all its varieties. For a correct choice of oxidant and reaction conditions it is probably important to find the way in which the crystal structure influences the oxidising power. Many papers have been published[15-19] on the crystal lattice of the various modifications of manganese dioxide, but little attention has been paid to the effect of the fine structure of this reagent on its oxidising properties. In some cases[20] an analogy has been noted between depolarising and oxidising activities.

The crystal structure of manganese dioxide has been studied by electron diffraction, X-ray diffraction, and electron microscopy. The X-ray pattern of manganese dioxide powder was found to have changed quite markedly after oxidation, but the change disappeared after six repetitions of the reaction. The oxidising power of manganese dioxide is almost independent of crystal size, although microcrystalline forms exhibit a higher initial rate of oxidation. Detailed data on the correlation between the effectiveness and the lattice structure of the manganese dioxides could not be obtained. It was found empirically that the more active forms comprise those obtained by oxidising manganese sulphate with potassium permanganate in alkaline medium[21], the γ-dioxide obtained by treating the permanganate with concentrated hydrochloric acid[22], and colloidal manganese dioxide[23].

Several methods have now been worked out for the preparation of active forms of manganese dioxide. Among all the forms which have been described, those prepared by the methods of Attenburrow (ACC†)[21] and of Rosenkranz (RSM)[24] have become most widely accepted and used. The first of these methods consists in the interaction of hot (80–90°) solutions of potassium permanganate and manganese(II) sulphate in the presence of caustic soda. The precipitate is separated, washed with distilled water, and dried at 100–120°. The activity of such a dioxide is not diminished by carrying out the synthesis under acid conditions[25] or after washing with dilute nitric acid. Ball, Goodwin, and Morton[6] prepared manganese dioxide (BGM) by the interaction of potassium permanganate and manganese(II) sulphate in neutral medium at room temperature. The activity of the BGM dioxide is somewhat lower than that of the RSM form prepared from the same reactants but at 80–90°. The oxidising activity of the latter is increased by washing it with 15% nitric acid[24]. Good results were obtained with manganese dioxide prepared by the pyrolysis of manganese(II) salts[13,26]. It is noteworthy that each form of active dioxide exhibits specific features in the oxidation of various classes of compounds[27].

Gritter and Wallace[26] consider that the forms of the dioxide prepared from potassium or barium permanganate and also from manganese chromate possess the highest activity. They suggest that oxidation is accelerated by the presence of traces of potassium permanganate or of higher oxides of manganese, included in the crystal lattice or adsorbed on the surface of the manganese dioxide. The decrease in activity of the ACC dioxide produced by washing with organic solvents is explained by the desorption of impurities from the surface. However, the results of X-ray examination and the ineffectiveness of the addition of small quantities of potassium permanganate to the manganese dioxide during the oxidation contradict these hypotheses. This conclusion is inconsistent also with the high activity of certain oxidants prepared by the pyrolysis of manganese(II) salts, which excludes any catalytic effect due to contamination with potassium permanganate. Neither naturally occurring forms of manganese dioxide nor the commercial product possess appreciable oxidising power in neutral medium. Gritter[26] made a comparative study of the activities of a series of dioxides by oxidising benzyl alcohol with the five most widely used forms, and showed that the oxidising power falls in the sequence

$$MnO_2: BGM^{24} > ACC^{21} > HBL^{15} > GW^{26}.$$

III. REACTION CONDITIONS

In the oxidation of alcohols to the corresponding carbonyl compounds this method may be preferred to Oppenauer's method[29]. The reaction is conducted under a great variety of conditions — with different solvents, over a fairly wide temperature range, in air and in nitrogen, and with the components present in various proportions — the starting material being in most cases shaken at room temperature with the finely ground dioxide in an inert solvent, or a

† For brevity and convenience the various forms of manganese dioxide will henceforward be denoted by the initial letters of the surnames of the authors who have published the methods of preparation.

solution being slowly passed through a column filled with the oxidant[30]. The time required for completion of the reaction varies from 10 min to 10 days and longer depending on several factors, among them being the activity of the dioxide, the solvent, the temperature of the reaction, the substance to be oxidised, and the relative proportions of the components.

1. Solvent

It has been found empirically that in many cases the rate and the direction of the reaction are affected by the choice of solvent. Many workers have noted the deactivating effect of certain solvents on manganese dioxide. Polar solvents, which are strongly adsorbed on the surface of the active dioxide, lower the activity of the oxidant. These include primarily aliphatic, especially tertiary, alcohols. Acetone and ethyl acetate also deactivate the oxidant, but considerably more slowly; in this case the activity of the manganese dioxide is easily restored by drying in a vacuum. Gritter[28] determined the rate of oxidation of unsaturated alcohols by manganese dioxide in various solvents, and showed that the fall in the rate of oxidation of alcohols in the sequence — petroleum ether > carbon tetrachloride > benzene — corresponds to an increase in the affinity of solvent and dioxide: benzene forms the most stable "complex" with the active centres on the surface, which prevents contact between oxidant and alcohol molecule. The solvent has been found to have a strong influence on the yields of the oxidation products, sometimes even changing the direction of the reaction. Thus Morton[6] showed that vitamin A in petroleum ether is converted almost quantitatively into retinene, whereas in diethyl ether it forms anhydrovitamin A. The solvents most widely used for oxidation in the cold are light petroleum ether, saturated hydrocarbons (pentane, hexane, cyclohexane), ethers, and acetone; ethyl acetate, dimethylformamide, acetonitrile, dimethyl sulphoxide, etc. are also used. The same solvents are employed, as well as water and pyridine, for reactions at high temperatures.

2. Time and Temperature of Reaction

The time and the temperature of the reaction depend on the activity of the manganese dioxide, the material to be oxidised, and the relative proportions of the components. The duration of oxidation at room temperatures varies within wide limits: whereas the transformation of $\alpha\beta$-unsaturated alcohols is usually complete at room temperature after a few minutes[31], the oxidation of alkylanilines[32] and the formation of steroid dienones[33] occupy 16–24 h. In order to shorten the reaction time, oxidation is frequently conducted at an elevated temperature in the boiling solvent, the water formed sometimes being removed by azeotropic distillation. The rate of the reaction and the time at which it is complete can be assessed qualitatively from the liberation of water. Raising the temperature to 70–120° markedly shortens the reaction time, but the yields, the purity of the product, and the selectivity of action of the oxidant are diminished. In some cases, especially when carbon–carbon bonds undergo cleavage during the oxidation, the reaction is complete at 80–100° after 10–20 h.[34,35] When the reaction is conducted at room temperature, vigorous agitation is necessary for maximum contact of the material with the surface of the dioxide in order to avoid local overheating.

3. Proportions of Reactants and Mode of Action of Active Manganese Dioxide

The oxidation of organic compounds in neutral solvents by active manganese dioxide is a heterogeneous reaction[6], so that the quantity of oxidant used is greatly dependent on the particle size of the dioxide. The particle size normally employed is 80–200 mesh. It is as yet impossible to determine theoretically, on the basis of known facts, the quantity of oxidant required. The ratio of substance to reagent usually varies within the range 1 : 5–20 by weight, and in some cases the excess of oxidant is increased to 1 : 50. The optimum proportions for the oxidation of $\alpha\beta$-unsaturated alcohols are 1 : 10 at room temperature, and 1 : 4–6 on boiling. In the opinion of many authors the ease of oxidation depends on the adsorbability of the given compound on the manganese dioxide. Ball et al.[6] consider this reaction to occur in three stages — adsorption of the substance from solution on the oxidant, oxidation, and desorption of the reaction product into the solution — from which it may be expected that more saturated compounds, which are more poorly adsorbed on the surface of the dioxide, should react at a lower rate. Results obtained by Harfenist[13] are fully consistent with Ball's conclusions. They showed that alcohols can be arranged in the sequence — conjugated polyene carbinols, benzyl and furfuryl alcohols, and vinyl- and ethynyl-carbinols — according to their ease of oxidation. However, the degree of adsorption is hardly the sole factor determining the reaction velocity.

Harfenist noted an interesting peculiarity in the oxidation of benzyl alcohols: the reaction does not usually go to completion, the product always being contaminated with the initial carbinol. In his view a permanent equilibrium is established at the surface of the dioxide between the starting material and the reaction product. Therefore oxidation proceeds successfully until a certain point is reached, at which the quantity of carbonyl compound formed attains a critical value, i.e. a concentration at which the final product begins to displace molecules of the initial alcohol from the dioxide surface. Henbest and Thomas[32] showed that only a small proportion of the oxygen in the manganese dioxide is consumed during oxidation. In their opinion water, bound to the manganese dioxide surface in the form of free hydroxyls, takes part in this reaction. Evans[8] points out that hydrated manganese dioxides contain available oxygen, the quantity of which has diminished by the theoretical amount after oxidation. The relative quantity of available oxygen in the various types of dioxide decreases in the sequence

$$MnO_2: GW > HBL > RSM > BGM > ACC.$$

The above sequence does not correspond to that based on the efficiencies of these forms of manganese dioxide in oxidising $\alpha\beta$-unsaturated alcohols. Consequently there is no direct link between the quantity of oxygen available in a sample of manganese dioxide and its oxidising power. If, however, we examine the dependence of rate of oxidation on the percentage contamination with other oxides of manganese, we find that the oxidising activity increases as the purity of the dioxide diminishes, the ACC dioxide forming an exception. Gritter[28] suggested that oxidising power is affected by the nature of the impurities present, especially cationic impurities. In his view, successful oxidation requires the presence on the manganese dioxide surface of centres of diminished electron density, capable of attracting the electron-rich oxygen of the alcoholic hydroxyl. The reaction velocity is determined by the number and type of these active centres.

The mechanism of oxidation by manganese dioxide has not yet been completely elucidated, and therefore the proposed schemes frequently contradict the experimental facts. Some investigators consider that compounds capable of forming more stable carbonium ions are more readily oxidised, but most authors deny the intermediate formation of a carbonium ion. Pratt[36] noted that the rate of oxidation of alcohols $C_6H_5CH(OH)-R$ increases roughly sevenfold as the radical R is varied in the sequence

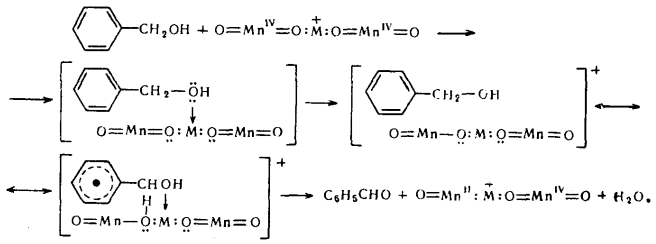
$$-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-C_6H_5;\ -\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3;\ -CH_2C_6H_5;\ -CH_3;\ H;\ -C_6H_5;\ -CH=CH-C_6H_5;\ -COC_6H_5.$$

Replacement of the hydrogen atoms in the methyl group by radicals leads to a successive decrease in the rate of oxidation. Branched radicals probably cause steric hindrance to adsorption of the oxidisable molecule on the surface of the active dioxide. Nevertheless, these substituents govern the stability of the free radicals. A change in structure of the substituents which increases the stability of the free radical is accompanied by an increase in reaction velocity. Thus primary aliphatic alcohols are oxidised more slowly than secondary alcohols, and the latter in turn more slowly than phenylmethanols.

The free-radical mechanism suggested by Pratt[36-38] for the oxidation of organic compounds by manganese dioxide, combined with the adsorption theory, is probably the most successful in explaining the general features of the oxidation:

$$R_2CHOH + O{=}Mn^{IV}{=}O \rightarrow R_2\dot{C}OH + HO{-}Mn^{III}{=}O \rightarrow$$
$$\rightarrow R_2\dot{C}{-}\acute{O} + HO{-}Mn^{II}{-}OH \rightarrow R_2CO + MnO + H_2O.$$

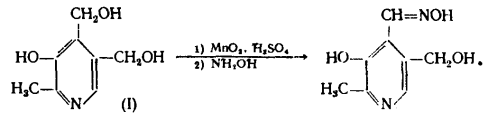
According to Gritter[28], in the course of the reaction the oxidisable substance forms a complex with the dioxide, ions of other metals, present as impurities in the oxidant, being involved in its formation:



An analogy can be traced between the oxidation of alcohols by manganese dioxide and the autoxidation of hydrocarbons in the presence of metal oxides, where similar complexes are probably formed[38].

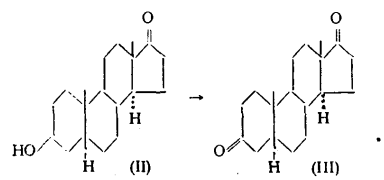
IV. OXIDATION OF ALCOHOLS

The oxidation of primary aliphatic alcohols with manganese dioxide in an acid medium was studied as early as the nineteenth century by Liebig[39], who converted ethanol into acetaldehyde with pyrolusite in sulphuric acid. β-Chloroacrylaldehyde[40], fluoroacetaldehyde[41,42], and several other aliphatic and aromatic carbonyl compounds have been obtained under similar conditions. The use has been described of manganese dioxide in acid medium for the oxidation of derivatives of vitamin A,[50] pyridoxol (I), and similar compounds[23,43-49]:

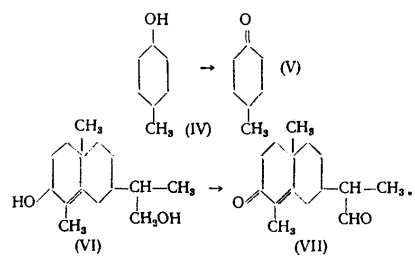


1. Oxidation of Saturated Alcohols in Neutral Medium

Comparison of the relative rates of oxidation of various types of alcohols shows that saturated alcohols are oxidised with great difficulty, while alcohols in which the hydroxyl is activated by a double or a triple bond, a system of conjugated bonds, an aromatic ring, or a carbonyl group are oxidised considerably more readily. The early work showed that neutral manganese dioxide (BGM) is inert towards primary and secondary aliphatic alcohols at room temperature. However, it was subsequently found that saturated alcohols can be oxidised to good yields of the corresponding aldehydes and ketones. In the oxidation with alkaline manganese dioxide (ACC) of ethanol, propan-2-ol, and isobutanol the yields of the carbonyl compounds reach 50%.[35] Gritter and Wallace[26] oxidised propan-1-ol and propan-2-ol under similar conditions, and obtained yields of 78% and 92% respectively. According to these workers, a long time or a high temperature is required for the reaction. The successful oxidation of saturated carbinols necessitates a large excess of the dioxide, as well as careful selection of the solvent[51]. For example, 3β-hydroxyandrostan-17-one (II) and its epimer when stirred in hexane or acetonitrile with ACC manganese dioxide for a day are converted into androstane-3,17-dione (III) in 99% yield:



Methylcyclohexanol (IV) in acetonitrile gives a 71% yield of 4-methylcyclohexanone (V):

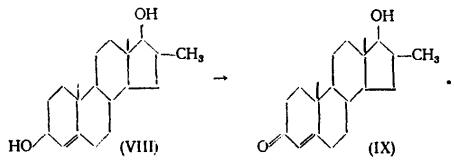


The analogue of α-santonin (VI)[52] is oxidised by manganese dioxide to the keto-aldehyde (VII).

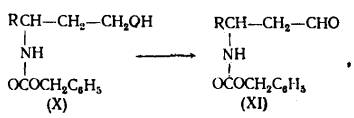
Thus the successful oxidation of saturated carbinols of various classes requires careful choice of reaction conditions and the form of the active dioxide. By means of active manganese dioxide it has proved possible to effect the oxidation of steroid alcohols[53], derivatives of gibberellic acid[54,55], alkaloids[56-59], cyclopropylmethanols[60], derivatives of tetrahydropyran-2- and -4-ols[14], bicyclo[3,3,0]-octanol[61], and other complex hydroxylated compounds[51,62-65].

The different positions of hydroxy-groups in polyols often permits selective oxidation of the hydroxyls[66-69]. A

clear example of such specific oxidation is provided by the preparation of 17α-hydroxy-16-methyl-13α,14β-androst--4-en-3-one (IX) from the corresponding 3,17-diol (VIII):[66]



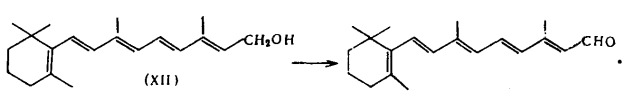
Here it is only the allylic hydroxyl which undergoes oxidation. Amino-alcohols and their benzyloxycarbonyl derivatives (X) are oxidised by the alkaline dioxide (ACC) with the formation of amino-aldehydes (XI):[70]



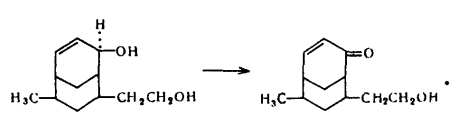
where R = C_6H_5, p-$CH_3OC_6H_4$.

2. Oxidation of αβ-Unsaturated Alcohols

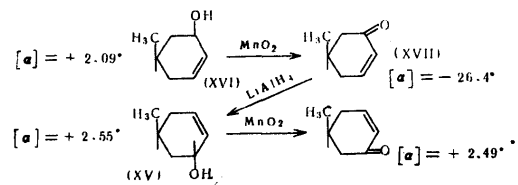
The first organic compound to be oxidised with active manganese dioxide in neutral medium was vitamin A_1 (XII), which contains a pentaene conjugated bond system and an allylic hydroxyl:



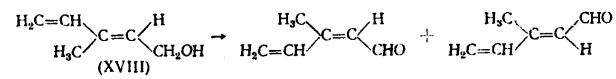
This work formed the start of a broad investigation into the oxidation of various unsaturated carbinols by manganese dioxide. During the following four or five years active manganese dioxide became firmly established as a convenient and efficient oxidant for the conversion of primary and secondary αβ-unsaturated alcohols into the corresponding carbonyl compounds. Detailed investigations of this reaction revealed certain relations between the structure and the ease of oxidation of the alcohols. Successful oxidation was found to require that the multiple bond in the unsaturated compounds should be located in the α-position with respect to the oxidisable hydroxyl. A break in conjugation sharply increases the inertness of the alcohols towards manganese dioxide. An example is provided by the oxidation of glycols containing only one allylic hydroxyl. Thus *cis*-8-2′-hydroxyethyl-6-methylbicyclo[3,3,1]non-3--en-2-ol (XIII) on treatment with active manganese dioxide gives only one oxidation product, 8-2′-hydroxyethyl-6--methylbicyclo[3,3,1]non-3-en-2-one (XIV):[71]



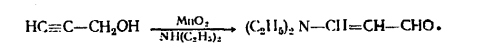
A characteristic feature of this reaction is the insensitivity of the carbon skeleton of unsaturated alcohols to the action of active manganese dioxide. In none of the work was cleavage of carbon–carbon bonds, change in the carbon skeleton, or allyl rearrangement noted, although these are so characteristic of many oxidations. However, some substances undergo stereochemical changes during oxidation. Cases have been reported[72] in which the angle of rotation of certain optically active alcohols changes on oxidation. The sign of rotation remains unchanged on treatment of (+)-*trans*-5-methylcyclohex-2-enol (XV) with manganese dioxide, whereas the (+)-*cis*-form (XVI) yields the *cis*--methylcyclohexenone (XVII), whose angle of rotation has the opposite sign:



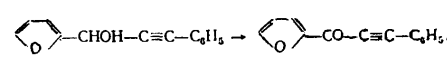
Sometimes the geometric configuration of the molecule changes during the reaction, with rearrangement of *cis*- and *trans*-substituents. Robeson[73] detected no change in the geometry of the molecule during oxidation of the geometric isomers of vitamin A_1 to the corresponding vitamin A aldehydes. Similar results were obtained by Wendler and Slates[74] in the oxidation of the *cis*- and *trans*-isomers of 2-ionylidene-ethanols. However, Boehm et al.[75,76] have observed *cis–trans* isomerisation in the transformation of pentadienols and pentenynols: *cis*-penta-2,4-dienol is oxidised by active manganese dioxide in pentane without geometric changes, whereas the *trans*-carbinol (XVIII) forms on oxidation a mixture of *cis*- and *trans*-isomers in the proportions 1 : 4:



Unsaturated alcohols containing one or more multiple bonds are very sensitive to oxidation by active manganese dioxide. This can be regarded as a classic method of synthesising unsaturated aldehydes and ketones, especially with the extremely labile naturally occurring polyene alcohols. Alcohols containing a double bond in the α-position to the hydroxy-group are oxidised by manganese dioxide to give a high yield of the corresponding carbonyl compounds, examples of this reaction being provided by the oxidation of allyl[26] and cinnamyl[36] alcohols to acrylaldehyde and cinnamaldehyde respectively. Good results have been obtained both with primary alcohols containing one double bond[77–82] or one triple bond[83] and with secondary alcohols[84–86]. The oxidation of prop-2-ynol (XIX) in the presence of diethylamine[87] gives the aminoacrylaldehyde (XX):



Alcohols in which the hydroxyl is activated by two multiple bonds[88–98] or by a multiple bond and an aromatic ring[99–102] are readily oxidised. Similarly, 1-fur-2′-yl--3-phenylprop-2-ynol (XXI) is converted into a high yield of 1-fur-2′-yl-3-phenylprop-2-ynone (XXII):[99]



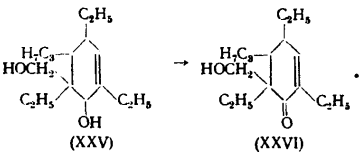
Active manganese dioxide has proved indispensable for the selective oxidation of such unstable compounds as the highly unsaturated polyene and polyenyne carbinols[103–114].

Thus treatment of dodec-2-ene-4,6,8,10-tetraynol (XXIII) with manganese dioxide gives dodec-2-ene-4,6,8,10-tetraynal (XXIV):[103]

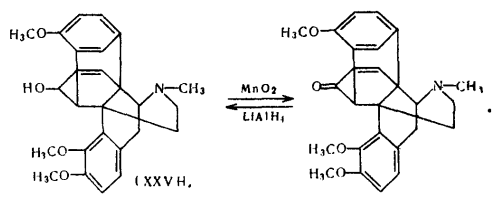
$$CH_3-(C\equiv C)_4-CH=CH-CH_2OH \rightarrow CH_3-(C\equiv C)_4-CH=CH-CHO.$$
(XXIII) (XXIV)

6-Methyl-8-phenylocta-3,5,7-trien-2-ol reacts similarly[104].

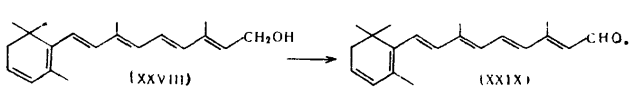
This method has been successfully applied to the oxidation of unsaturated cyclic carbinols[115-127]:


(XXV) (XXVI)

The cyclohexenone (XXVI) is obtained in 80% yield by oxidation of the corresponding alcohol (XXV) in cyclohexane at 20°.[115] Active manganese dioxide has been used for the oxidation of hydroxy-groups in certain alkaloids and other natural products[128-140]. This has enabled their structure to be established, e.g. in the case of flavothebaone (XXVII):[129]

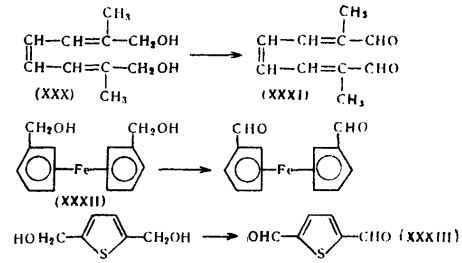

(XXVII)

The exceptionally mild action of the active dioxide has enabled it to be used for the preparation of difficultly accessible carbonyl derivatives of vitamin A. In this case none of the known oxidants gave positive results. Numerous papers have been published on the synthesis of the corresponding aldehyde from vitamin A_1,[6,30,141] α- and β-ionylideneacetaldehydes[142-145], and β-ionone[146] by means of manganese dioxide in inert solvents at room temperature. A similar conversion is characteristic also of vitamin A_2 (XXVIII), which is readily oxidised to the aldehyde (XXIX),[147-149] and also of 8,9-dehydrovitamin A,[21] neovitamin A,[150] and several other similar compounds[151-155]:

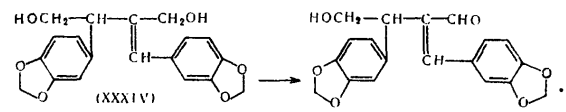

(XXVIII) (XXIX)

Vitamin A_1 aldehyde has been prepared also from vitamin A_1[156] and β-carotene[157] by oxidation with air in the presence of manganese dioxide. The use of these methods has enabled a convenient and cheap process to be developed for obtaining vitamin A aldehyde identical with the product isolated from the retina.

In the oxidation of polyols several reactions are possible, involving one or more hydroxyls depending on their degree of activation by multiple bonds, or accompanied by cleavage of skeletal carbon bonds (under more severe conditions). Special interest attaches to the synthesis of polyene and aromatic dialdehydes and diketones[158-172]. An example is provided by the oxidation of 2,7-dimethylocta-2,4,6-triene-1,8-diol (XXX)[164] in 94% yield to the corresponding dialdehyde (XXXI), of 1,1′-bishydroxymethylferrocene (XXXII),[171] and of 2,5-bishydroxymethylthiophen (XXXIII):[172]

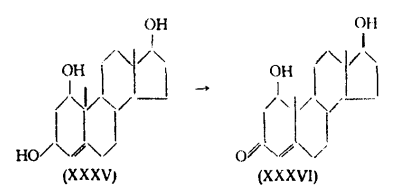

(XXX) (XXXI) (XXXII) (XXXIII).

Glycols in which the hydroxy-groups are activated to different extents behave somewhat differently. Thus several publications have indicated the possibility of oxidising only an allylic type of hydroxyl[173-175]. A break in the chain of conjugation in an unsaturated bond system, even by only one carbon atom, for example, as in (XXXIV),[173] markedly decreases the rate of oxidation:


(XXXIV)

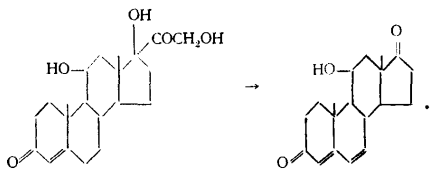
Barakat et al.[35] were able to obtain benzil and *pp′*-dimethoxybenzil in good yields from the corresponding α-hydroxy-ketones. This work also showed that ethylene glycol, glycerol, mannitol, and inositol are oxidised to carbon dioxide and water when boiled with an aqueous suspension of active manganese dioxide. The oxidation of hydroxy-acids is also anomalous: reaction is very rapid, and is accompanied by the evolution of carbon dioxide, aldehydes and ketones being formed containing one fewer carbon atoms than in the initial acid. Under milder conditions esters of hydroxy-acids undergo the usual type of oxidation[176-179].

The specificity of the action of active manganese dioxide has enabled it to be used for the oxidation of several steroid hydroxy-compounds[180-203]. The reaction goes mainly by the usual route, with conversion of only an allylic hydroxyl. Androst-4-ene-1β,3β,17β-triol (XXXV) is oxidised, in propan-2-ol at room temperature, to 1β,17β-dihydroxyandrost-4-en-3-one (XXXVI):[180]


(XXXV) (XXXVI)

It is advisable to conduct the reaction at room temperature in order to ensure that the structure of the molecule shall be preserved. Otherwise, oxidation of the hydroxyl may be accompanied by dehydrogenation of the olefinic to a diene system, migration of double bonds[204-208], and even rupture of carbon–carbon bonds.

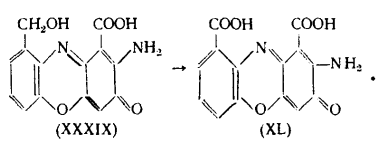
Special interest attaches to the oxidation of steroid 5-en-3β-ols, which in hot benzene are converted into 4,6-dienones[33], whereas in dimethylformamide or pyridine at 20° they give 4-en-3-ones, although the rate of reaction is not very high[51]. This extends the possibilities of synthesis of steroid products. Manganese dioxide in boiling chloroform splits off the side-chain in dihydroxy-acetonyl steroid alcohols to give 17-oxosteroids[34]. Hydrocortisone (XXXVII) is converted into 11β-hydroxyandrosta-4,6--diene-3,17-dione (XXXVIII):[209]



(XXXVII) (XXXVIII)

3. Oxidation of Aromatic Alcohols

The oxidation of benzyl alcohols and similar compounds by active manganese dioxide has been studied in some detail. As already mentioned, this oxidant has been regarded as ineffective for these alcohols. These views have now been completely refuted, and manganese dioxide has become widely used in the synthesis of aromatic aldehydes and ketones. Turner[12] was able to effect the mild oxidation of diphenylmethanol, xanthen-9-ol, furoin, 1-1'-naphthylethanol, tetrahydrophenanthren-1-ol, and several other alcohols. During recent years the successful oxidation has been accomplished of substituted benzyl alcohols[210-215], 2- and 4-hydroxymethylindoles[216,217], hydroxymethylferrocene[218], triazolylmethanols[219], secondary phenylmethanols[220,221], 1-thienylethanol[222], 1-furylalkanols[83], 2-hydroxyarylalkylbenzimidazoles[223], 4-pyranylmethanols[224], etc. The oxidation of benzyl alcohols usually goes readily, and stops at the carbonyl stage. Only one example has been reported in which the corresponding acid could be isolated as the main product: 2-amino-9-hydroxymethyl-3-oxophenoxazine-1-carboxylic acid (XXXIX), with manganese dioxide in chloroform at room temperature, gives the dicarboxylic acid (XL) as the sole product[225]:

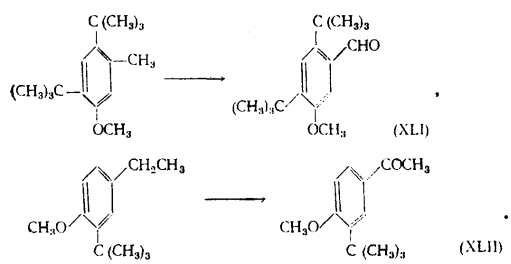


(XXXIX) (XL)

Insufficient study has hitherto been made of the mechanism of the oxidation of benzyl alcohols and similar compounds. Pratt[36] established that electron-acceptor properties of *para*-substituents in phenylmethanols have considerably less effect on their rate of oxidation than would have been expected on the hypothesis of a carbonium-ion mechanism. Moreover, Gritter and Wallace[28] have shown that methyl, methoxyl, and nitro-groups in the *ortho*-, *meta*, and *para*--positions always increase the rate of oxidation of the phenylmethanols in comparison with that of unsubstituted benzyl alcohol. This phenomenon is explained by a free-radical mechanism for the reaction. The insignificant effect of the nature of substituents becomes understandable, for radical reactions are accelerated by both electron-acceptor and electron-donor substituents. This mechanism is confirmed by the decrease in the rate of oxidation produced by the addition of diphenylamine. In a study of the oxidation of the alcohols $C_6H_5CH(OH)-R$ (where R = H, Alk, C_6H_5, $C_6H_5CH_2$, $C_6H_5CH{:}CH$, C_6H_5CO, etc.), Pratt explained the differences in the rates of oxidation of the α-substituted benzyl alcohols as due to two effects — the steric effect of substituents capable of preventing rapid adsorption of the alcohol on the surface of the active manganese dioxide, and the effect of the stabilisation of free radicals formed in the first stage of oxidation. Similar results were obtained by Gritter.

V. OXIDATION OF HYDROCARBONS

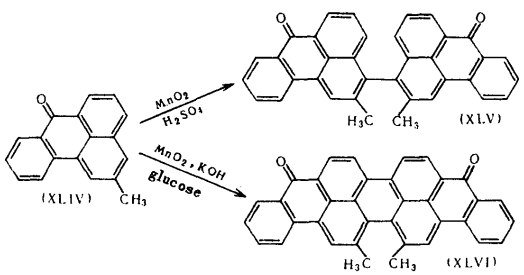
For a long time a great deal of attention has been paid in the chemical literature to the problem of the oxidation of alkylbenzenes. Among oxidising agents used for this reaction an important place is occupied by natural manganese dioxide, pyrolusite. In all cases oxidation is found to involve only the alkyl substituent in the benzene ring. Thus Fel'dman[226] heated 2,4-dichlorotoluene in the presence of pyrolusite and 58% sulphuric acid at 80° for 16–19 h, and obtained an 80% yield of 2,4-dichlorobenzoic acid, whereas *p*-nitrotoluene gives *p*-nitrobenzoic acid[227]. Alkylpyridines undergo similar oxidation[228]. When toluene is nitrated with a mixture of sulphuric and nitric acids in the presence of manganese dioxide, a mixture of *p*-nitrotoluene and 2,4-dinitrobenzaldehyde is formed[229]. It has been suggested[230] that terephthalic acid can be prepared by the oxidation of *p*-cymene with manganese dioxide in sulphuric acid. Thus the aromatic ring and certain functional substituents remain unchanged during the reaction, whereas a methyl group is converted into carbonyl or carboxyl depending on the conditions. The reaction conditions can be so chosen that oxidation is halted at the carbonyl stage. Lifshits[231] obtained a mixture of benzyl alcohol and benzaldehyde by the interaction of toluene and manganese dioxide in the presence of sulphuric acid. Carpenter et al.[232] were able to oxidise substituted methyl- and ethyl-benzenes to the corresponding benzaldehyde (XLI) and acetophenone (XLII) respectively:



Recently Hüttel and Christ[233] have proposed a new method for synthesising αβ-unsaturated carbonyl compounds (XLIII) by oxidising palladium dichloride–alkene complexes with various reagents, including manganese dioxide in an acid medium:

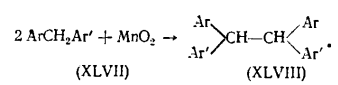
Manganese dioxide is used also for the oxidative dimerisation and even polymerisation of aromatic hydrocarbons. Travkin[234] heated 2-naphthol with manganese dioxide at

260° for 3 h, and obtained a quantitative yield of binaphthyl-2,2′-diol. Oxidation[235] of 2-methylmesobenzanthrone (XLIV) with manganese dioxide in sulphuric acid at 0–5° gives a 78% yield of 2,2′-dimethyl-3,3′-bibenzanthryl-7,7′-dione (XLV), whereas in alkaline medium containing glucose the product is 16,17-dimethylviolanthrone (XLVI):



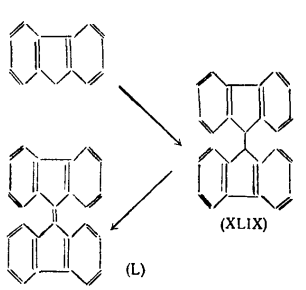
A convenient method for synthesising *p*-polyphenyls from benzene has been worked out by Kowacic[236]: the polyphenyls are formed by the action of manganese dioxide, copper(II) chloride, lead dioxide, and other oxidising agents in the presence of catalytic quantities of aluminium chloride.

The oxidative dimerisation of diarylmethanes (XLVII) by active manganese dioxide in neutral medium can be regarded as the same type of reaction[37]:



Three types of product — (1) tetra-arylethanes (XLVIII), (2) tetra-arylethylenes, or (3) diaryl ketones — may be formed depending on the conditions. Pratt made a detailed study of this process, and found it to be a general reaction with all symmetrical and unsymmetrical diarylmethanes, the rate of the reaction and the yield of tetra-arylethylenes depending on the electronic properties of the aryl ring.

The oxidation of *pp*′-dinitrodiphenylmethane, fluorene, and xanthen in a mixture of benzene and biphenyl at 211° is accompanied by the liberation of double the theoretical quantity of water. This suggests that, in the course of oxidation, tetra-arylethanes are dehydrogenated to the corresponding ethylenes, which were isolated in 15–30% yields. In order to demonstrate the formation of tetra-arylethylenes at the expense of tetra-arylethanes, 9,9′-bifluorenyl (XLIX) was converted into a 75% yield of 9,9′-bifluorenylidene (L) by the same method:



In view of the great stability of diarylmethane radicals, Pratt suggested a free-radical mechanism of oxidation:

$$Ar_2CH_2 + O{=}Mn{=}O \rightarrow Ar_2\dot{C}H + HO{-}Mn{=}O, \quad (1)$$

$$Ar_2CH_2 + HO{-}Mn{=}O \rightarrow Ar_2\dot{C}H + HO{-}MnOH, \quad (2)$$

$$2\,Ar_2\dot{C}H \rightarrow Ar_2CH{-}CH{\cdot}Ar_2. \quad (3)$$

This scheme is confirmed by the increase in rate of oxidation in the sequence — diphenylmethane, 1-benzylnaphthalene, *p*-benzylbiphenyl, di-*p*-biphenylylmethane — which corresponds to increasing stability of the corresponding free radicals. Dehydrogenation of tetra-arylethanes to the ethylenes may pass through analogous stages. Good yields of the former were obtained by stirring with a fourfold excess of manganese dioxide by weight in a 20 : 1 biphenyl–benzene mixture at 211°. The yields of tetra-arylethanes diminish with fall in temperature, although the theoretical quantity of water is liberated.

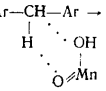
Simultaneous formation of diaryl ketones was also noted, their yields increasing with fall in temperature and increase in the quantity of active dioxide. The corresponding diarylmethanols are probably intermediate products in the oxidation of diarylmethanes to diaryl ketones. Manganese dioxide is normally used for the abstraction of hydrogen atoms, the oxidation of hydrocarbons to ketones representing a rare though not unique case of the introduction of oxygen into the carbon skeleton[227]. A possible source of hydroxy-groups is hydrated manganese dioxide, on whose surface hydroxyls are present as free radicals or as HO–Mn=O. The reaction can then be written

$$Ar_2\dot{C}H + HO{-}Mn{=}O \rightarrow Ar_2CHOH + MnO. \quad (4)$$

Reaction (4) together with reaction (1) explains the increased yield of ketones when the solvent is not distilled off during the reaction and when the latter is conducted at lower temperatures, since active manganese dioxide is rapidly dehydrated during the azeotropic distillation of water and solvent, which diminishes the possibility of attack by a hydroxyl on the free radical. At the same time, a reaction in which water and solvent are distilled off promotes the desorption and recombination of radicals, i.e. reaction (3). Thus

$$Ar_2\dot{C}H + HOMnO \rightarrow Ar_2CHOH + MnO,$$

$$Ar{-}CH{-}Ar \rightarrow Ar{-}CHOH{-}Ar + MnO,$$



$$Ar_2CHOH \rightarrow Ar_2CO + H_2O.$$

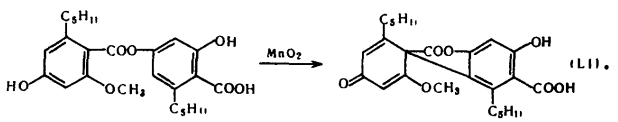
The above mechanism is confirmed by the oxidation of diphenylmethane with manganese dioxide which has first been dehydrated by being boiled in toluene. When the hydrocarbon is oxidised with this dioxide in the absence of solvent, the yield of benzophenone falls from 74% to 2%. Since the dioxide undergoes still greater dehydration in reaction with a solvent at high temperatures, it follows that in this case practically no ketone will be formed.

VI. OXIDATION OF PHENOLS

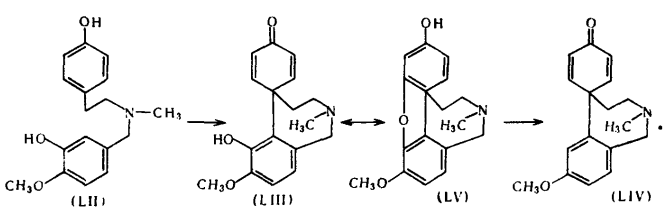
In recent years several successful syntheses, involving the oxidative linking of phenols, have been made of important natural products from readily available and inexpensive substances[238-241]. This method is based on the free-radical coupling of certain phenol derivatives, the reaction

being regarded as analogous to biochemical processes occurring in the living cell. Various oxidants convert phenols into mono- or di-radicals, which can then react intramolecularly or dimerise, new carbon–carbon, carbon–nitrogen, or carbon–oxygen bonds being formed. Active manganese dioxide occupies a special place[241] among the numerous oxidising systems (lead dioxide, potassium hexacyanoferrate(III), hydrogen peroxide, etc.) employed for this purpose.

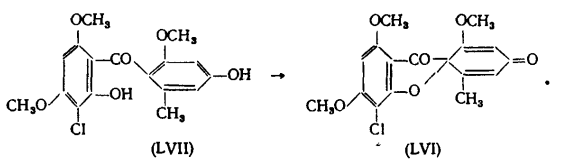
Scott and Davidson[242,243] have synthesised picrolichenic acid (LI), previously isolated from *Pertusaria amara*:



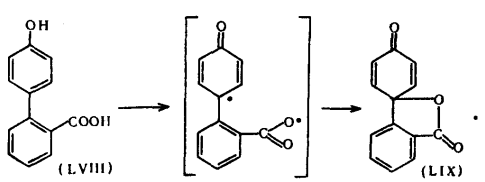
Under similar conditions Barton and Kirby[244,245] have obtained from *p*-hydroxy-*N*-(3-hydroxy-4-methoxybenzyl)-*N*-methylphenethylamine (LII) the alkaloid galanthamine (LIII), which can be further oxidised via (LV) to narwedine (LIV):[246,247]



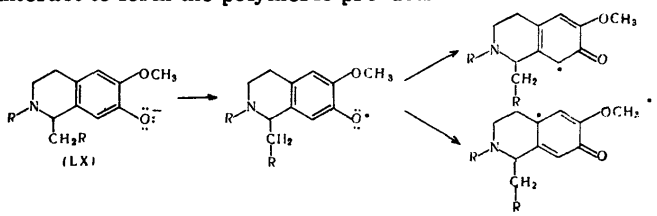
Several morphine alkaloids[248] and geodin[241] have been synthesised by a similar scheme. A new carbon–carbon bond is formed also in the oxidation of bisphenols[249]. In other cases the oxidative coupling of phenols leads to the formation of a carbon–oxygen bond. This can be seen in the synthesis of depsidone and diploicin[250,251] and of dehydrogriseofulvin (LVI)[252,253] from 3-chloro-2,4′-dihydroxy-2′,4,6-trimethoxy-6′-methylbenzophenone (LVII):



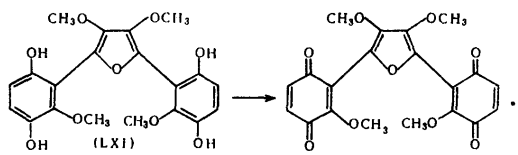
Oxidation of 4′-hydroxybiphenyl-2-carboxylic acid (LVIII) with manganese dioxide in ether[254] gives a 25% yield of phthalan-1-spiro-1′-cyclohexadiene-3,4′-dione (LIX):



Interaction of phenolic tetrahydroisoquinoline bases with active manganese dioxide at room temperature results in formation of the isoquinoline system[241,255]. At higher temperatures hydrogen is detached from the hydroxyl with formation of polymeric products. The phenoxide ion (LX) is converted into a mixture of radicals having their unpaired electron on the oxygen atom or in the *ortho*- or *para*-positions of the cyclohexadiene ring, and these radicals then interact to form the polymeric products[256,257].

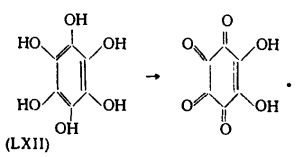


Oxidation of the mono- and di-adducts of 3,4-dimethoxyfuran with acetylbenzoquinone (LXI) involves conversion of the 2,5-dihydroxyphenyl into *p*-quinonoid substituents[258]:



These reactions have been used for the purification of industrial waste waters from *p*-t-butylphenol, bishydroxyphenylpropane, and other phenols[259].

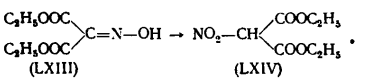
The oxidation of phenols with manganese dioxide in acid and alkaline media has been known for a long time. As early as the nineteenth century Clark[260] oxidised quinol to *p*-benzoquinone with manganese dioxide in sulphuric acid. The most interesting of recent investigations is that by Fatiadi[261] on the oxidation of benzenehexaol (hexahydroxybenzene) (LXII) with a specially prepared highly active dioxide in alkaline medium:



VII. OXIDATION OF AMINES

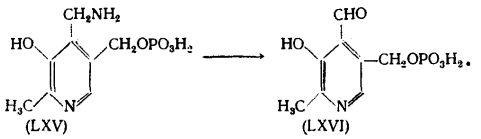
An important field for the application of active manganese dioxide is the oxidation of various amino-compounds. This reaction occurs in several ways, and covers a wide range of compounds containing nitrogen. Their interaction with manganese dioxide may involve oxidation of alkyl groups, cleavage of carbon–carbon bonds, and dehydrogenation of carbon–carbon and carbon–nitrogen bonds. The process may be either unimolecular or bimolecular.

The oxidation of amino-compounds with manganese dioxide in acid medium is widely used for the synthesis of various classes of compounds. An example is provided by the oxidation of aniline with the natural dioxide in acid medium to form *p*-benzoquinone[262]. In dilute acetic acid the oxime (LXIII) is readily converted into the nitro-compound (LXIV):[263]



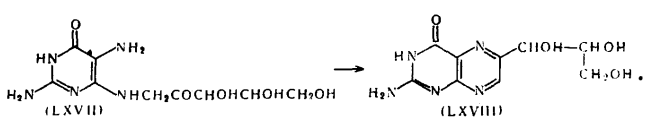
3-(2-Piperidyl)pyridine (anabasine) on oxidation with manganese dioxide in sulphuric acid gives a 45% yield of nicotinic acid[264]. Isonicotinic acid has been obtained by the oxidation of 4-ethylpyridine[228] and 4-methylpyridine[265].

When pyridoxamine (LXV) is subjected to prolonged heating with manganese dioxide in water containing sulphuric or phosphoric acid[45,266], the aminomethyl group is converted into an aldehyde group (LXVI):



(LXV) (LXVI)

Among recent work mention must be made of the paper by Lagowski and Forrest[267] describing the preparation of 2-amino-3,4-dihydro-4-oxo-6-(L-*erythro*-1,2,3-trihydroxypropyl)pteridine (LXVIII) by oxidation of the 1-pyrimidinylamino-1-deoxypentulose (LXVII):



(LXVII) (LXVIII)

In 1955 Highet and Wildman[14] accomplished the oxidation of benzylamine, *N*-methylbenzylamine, and *N*-methylpiperonylamine with manganese dioxide in chloroform. The infrared spectrum of the oxidation product of benzylamine was almost identical with that of hydrobenzamide, which confirms the intermediate formation of the imine (LXIX):

$$R{-}CH_2NH{-}CH_3 \rightarrow R{-}CH{=}N{-}CH_3.$$

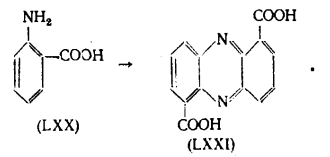
(LXIX).

Tertiary amines do not undergo this reaction, which was subsequently extended to anilines, *N*-alkylanilines, hydrazines, and hydrazones of carbonyl-containing compounds.

Great attention has been paid to the oxidation of various ring-substituted anilines to azobenzenes. Various oxidising agents — including per-acids[268], diacetoxyiodobenzene[269], sodium borate[270], lead tetra-acetate[271], etc. — have previously been used for this purpose. The simplicity of the oxidation procedure and the availability of manganese dioxide have made this method the most widely used in the synthesis of azobenzenes. Barakat et al.[35] investigated the oxidation of aniline, *o*- and *p*-chloroanilines, *p*-toluidine, 1- and 2-naphthylamines, and also *o*-, *p*-, and *m*-nitroanilines with alkaline manganese dioxide in petroleum ether. Aniline and methyl- and chloro-anilines gave the corresponding azobenzenes in excellent yields.

Wheeler and Gonsalez[272] derived several general rules from a study of the oxidation with active manganese dioxide of a series of ring-substituted anilines. One of their main conclusions was that the electronic character of the substituent has no appreciable effect on the reaction velocity or the yield of the oxidation product, although a slight electronic effect is nevertheless present. Thus *para*-substituted anilines react somewhat faster than other isomers. In a series of halogenoanilines the rate of oxidation falls in the sequence F > Cl > Br > I. 3,5-Dichloro- and 2,6-dimethoxy-anilines react normally, as does 3-chloro--4,6-dimethoxyaniline. However, several substituted nitroanilines — 2-iodo-4-nitro-, 2,6-di-iodo-4-nitro-, and 2-methyl-5-nitro-anilines — do not react with manganese dioxide. This cannot be explained by the electronic effects of the substituents, for in some cases the nitro-group facilitates oxidation. One possible explanation is that the nitro-group itself may be adsorbed on the surface of the manganese dioxide, and thereby prevent oxidation of the amino-group. Therefore 3,5-dichloro-4-nitroaniline, in which adsorption of the nitro-group is impeded by the neighbouring chlorine atoms, forms the azobenzene to a slight extent, whereas 3,5-dichloro-2-nitroaniline, in which the electronic effect of the chlorine atoms is the same as in the 4-nitro-isomer, is completely incapable of being oxidised.

Carboxyl resembles the nitro-group in having an unfavourable effect. The diminished polarity of the carboxyl in ethyl *p*-aminobenzoate, and the consequently diminished adsorbability of carboxyl on the manganese dioxide surface, make it possible to obtain a low yield of diethyl azobenzene--*pp'*-dicarboxylate. It has recently been found[273] that anthranilic acid (LXX) is oxidised in low yields to phenazine-1,6-dicarboxylic acid (LXXI):



(LXX) (LXXI)

The relatively minor influence of the nature of the substituents in the oxidation of amines can be regarded as an indication that this reaction has a free-radical mechanism. The formation of free radicals as intermediate products in the oxidation of amines has been suggested by Henbest and Stafford[274]. It must not be overlooked, however, that adsorption phenomena may mask the influence of the electronic structure of substituents in the actual oxidising step. Thus the oxidation of primary aromatic amines is a bimolecular adsorption dehydrogenation of the amino-group.

This idea has been developed by Pratt and McGovern[38], who have studied the oxidation of *N*-benzylanilines (LXXII) to benzylideneanilines (LXXIII):

$$X{-}C_6H_4CH_2NH{-}C_6H_4{-}X' \xrightarrow{MnO_2} X{-}C_6H_4CH{=}N{-}C_6H_4{-}X'.$$

(LXXII) (LXXIII)

Since an important part is played by the adsorption of anilines on the surface of the manganese dioxide, *ortho*-substituted benzylanilines react more slowly than the *para*-substituted isomers, and the *o*-methoxy-derivatives are oxidised far more slowly than the *o*-methylated compounds, since the former contain a more bulky substituent. Furthermore, the rate of oxidation of benzylanilines is independent of the electronic characteristics of the substituents.

Hydrazobenzenes (LXXIV) are extremely readily dehydrogenated to azobenzenes (LXXV) in high yields:

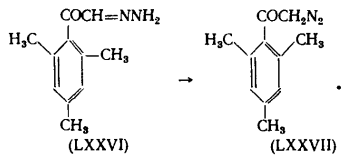
$$X{-}C_6H_4{-}NH{-}NH{-}C_6H_4{-}X \rightarrow X{-}C_6H_4N{=}N{-}C_6H_4X.$$

(LXXIV) (LXXV)

The rate of this oxidation is hardly affected at all by substituents.

The oxidation of hydrazones of carbonyl compounds by manganese dioxide represents a unimolecular dehydrogenation of the amino-group. Barakat showed that the active dioxide is able to oxidise hydrazones of ketones to azines. The appearance of a violet colour in the solution suggests formation of a diazo-compound as an intermediate stage in the oxidation. Schroeter[275] reported that active manganese dioxide oxidised hydrazones of substituted benzophenones to diazo-derivatives, though in lower yields than with oxidation by silver oxide. The dihydrazone of dibenzoylbenzene is converted under these conditions into a bisdiazo--compound[276,277]. Morrison and Danishefsky[278] used alkaline manganese dioxide to prepare diazo-ketones from

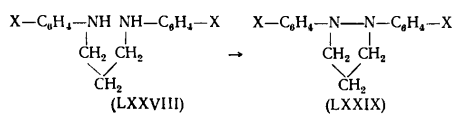
monohydrazones of diketones and keto-aldehydes. Mesitylglyoxal hydrazone (LXXVI) when shaken with the active dioxide forms diazomethyl mesityl ketone (LXXVII):



(LXXVI) (LXXVII)

Diekmann[279] obtained by means of manganese dioxide a 55% yield of bisphenylsulphonyldiazomethane from the hydrazone of bisphenylsulphonylformaldehyde. A similar reaction has been described with dihydrazones[280], where it is probable that diazo-compounds are also intermediate products[281]. Phenylhydrazides of acids form, with manganese dioxide in dilute acetic acid, aromatic hydrocarbons[282,283], while methylhydrazine in the presence of alkali forms ethane[284].

The oxidation of trimethylenediamines also consists in the oxidative dehydrogenation of the two amino-groups with subsequent intramolecular cyclisation to a pyrazoline. Wittig[285] obtained from *NN'*-diphenyltrimethylenediamine a 31% yield of 1,2-diphenylpyrazolidine. A more detailed study of this reaction has been made by Daniels and Martin[286], who found that the oxidation depends to a considerable extent on the type of active dioxide used. The conversion was investigated of a large number of 1,3-bisarylaminopropanes (LXXVIII) into the corresponding 1,2-diarylpyrazolidines (LXXIX):



(LXXVIII) (LXXIX)

In the case of *NN'*-di-*p*-methoxyphenyltrimethylenediamine the product is *pp'*-dimethoxyazobenzene[287]. Nevertheless, the corresponding ethoxy-derivative reacts normally, with formation of a pyrazolidine ring. *NN'*-Dialkyltrimethylenediamines do not undergo this reaction.

N-Alkylanilines undergo a different type of reaction with active manganese dioxide, alkyl and methylene groups in the amines being involved. Henbest et al.[32,288] studied the oxidation of *N*-alkyl- and *NN*-dialkyl-anilines with a large excess of manganese dioxide (ratio of reactants 1 : 50–100), and showed that three types of reactions could occur in this case — (*a*) formation of an amide

$$\rangle N{-}CH_3 \rightarrow \rangle N{-}CHO;$$

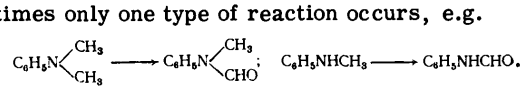
(*b*) dealkylation with formation of an aliphatic aldehyde

$$\rangle N{-}CH_2R \rightarrow \rangle NH + RCHO;$$

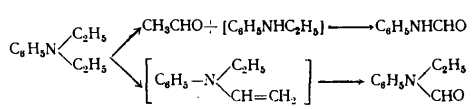
(*c*) dehydrogenation at an alkyl C–C bond followed by cleavage of the resulting enamine

$$\rangle N{-}CH_2CH_2R \rightarrow \left[\rangle N{-}CH{=}CH{-}R\right] \rightarrow \rangle NCHO + RCHO.$$

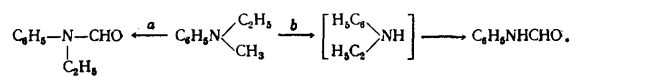
Sometimes only one type of reaction occurs, e.g.



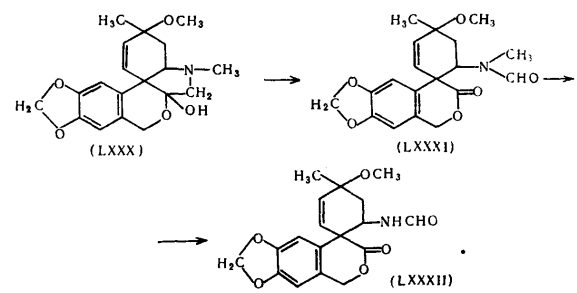
With diethylaniline the course of the reaction is more complicated:



Enamines are readily cleaved by manganese dioxide, as has been shown by the oxidation of *NN*-dibenzylstyrylamine to *NN*-dibenzylformamide[288], and also in the oxidation of sporidesmin[289] with a freshly prepared active dioxide. Introduction of a *p*-methyl group was found to facilitate the reaction, whereas a *p*-nitro-group impeded it. Small quantities of azobenzenes are formed as side-products in the oxidation of *N*-ethyl-*N*-methyl- and *NN*-diethyl-anilines. *N*-Ethyl-*N*-methylaniline yields both *N*-ethylformanilide and formanilide itself:

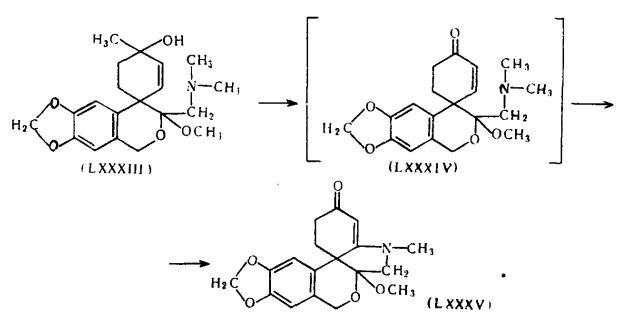


1,4-Diphenylpiperazine forms *NN'*-diformyl-*NN'*-diphenylethylenediamine, the process consisting in oxidative cleavage of a carbon–carbon single bond. This reaction is of great importance, for it represents the only known method of converting ethylenediamines into *N*-formyl derivatives. It has been used for the oxidation of tazettine to tazettamide, and of dihydrotazettine to dihydrotazettamide[290], and also in analytical practice for the determination of ethyl groups in diethylamino-compounds[291]. Japanese workers[292,293] have been able to isolate from oxidation of the alkaloid tazettine (LXXX), besides tazettamide (LXXXI), products of further oxidation, including *N*-desmethyltazettamide (LXXXII):



(LXXX) (LXXXI) (LXXXII)

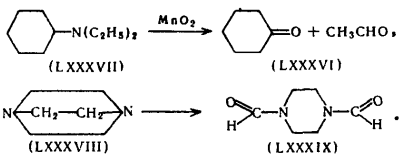
It is interesting that oxidation of a similar dimethylamino-derivative (LXXXIII)[294] produces, instead of the expected cyclohexenone (LXXXIV), oxidative elimination of one *N*-methyl group with cyclisation to dihydro-*O*-methyltazettinone (LXXXV):



(LXXXIII) (LXXXIV) (LXXXV)

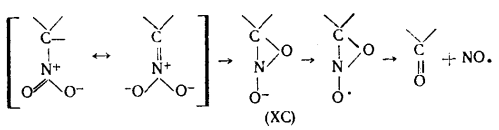
In some cases oxidation with manganese dioxide does not affect a dimethylamino-group[295]. With dialkylbenzylamines[296] the reaction consists in oxidation of the methylene group of the benzyl radical with detachment of the amino-group, various yields of benzaldehyde being formed in all cases. Tribenzylamine reacts very slowly, probably owing to steric hindrance to adsorption on the surface of the dioxide. Dialkylcyclohexylamines are transformed in good

yields into cyclohexanone (LXXXVI), the diethyl derivative (LXXXVII) being oxidised also at the ethyl group to form acetaldehyde[288]. Triethyleneamine (LXXXVIII) is oxidised with cleavage of a C–C bond to 1,4-diformylpiperazine (LXXXIX):

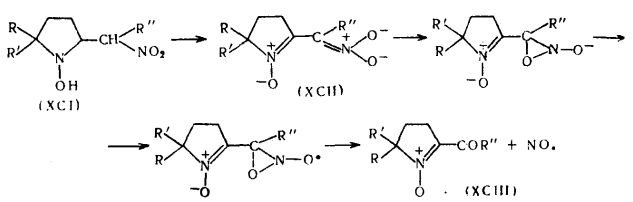


Active manganese dioxide has been successfully used for dehydrogenation at a carbon–nitrogen bond in nitrogen heterocycles. Thus tetrahydroquinazoline derivatives are converted into good yields of the corresponding dihydroquinazolines[297], and similarly pyrrolidine into pyrroline derivatives[298].

The oxidative elimination of nitric oxide from nitro-compounds represents a special case of the use of active manganese dioxide. The literature contains examples of analogous reactions in the presence of per-acids and quinones. Thus Jones[299] showed that 4-nitro-2,6-diphenylphenol when heated with an oxidising agent loses nitric oxide and is converted in good yield into 2,6-diphenyl-1,4-benzoquinone. Such reactions are regarded as taking place according to the following scheme



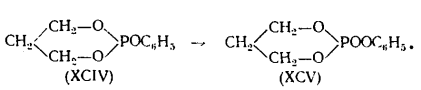
The oxaziran ring (XC), which is formed when a C=N double bond is present, breaks down to form a carbonyl compound and nitric oxide. Bowering et al.[300] have shown that a similar reaction is possible with 2-nitroalkylhydroxylamines:



Ethyl 1-hydroxy-2-methyl-5-(1-nitroethyl)pyrrolidine-2-carboxylate (XCI; R = $COOC_2H_5$, R′ = R″ = CH_3) is oxidised to the pyrroline anion (XCII), which is then converted according to the above scheme into the *N*-hydroxypyrroline (XCIII). The reaction takes place in petroleum ether at room temperature and lasts 4–6 h.

VIII. OXIDATION OF OTHER CLASSES OF COMPOUNDS

Active manganese dioxide is a good oxidising agent for tervalent phosphorus compounds. This reaction was first used for the conversion of triphenylphosphine into triphenylphosphine oxide[35]. Phenyl trimethylene phosphite (XCIV), obtained by reaction of triphenyl phosphite with trimethylene glycol, gives when shaken with manganese dioxide a 56% yield of the corresponding phosphate (XCV):[301]



Kabachnik and his coworkers have described the oxidation by means of active manganese dioxide of tertiary vinylphosphines[302], dibutyl-2-piperidinoethylphosphine, and dibutyl 2-piperidinoethyl phosphite to the corresponding oxides[303]. They have also studied the oxidation of vinyl-, allyl-, and vinylphenyl-phosphonous esters[304]. In all these cases reaction takes place readily, to give high yields without the formation of side-products.

Edwards and Stenlake[305] successfully used manganese dioxide for the oxidation of alkyl sulphides, and a paper has recently been published on the oxidation of various thiols with this oxidant[306].

Several papers have been published on the action of manganese dioxide on carbohydrates[307,308] — aldohexoses (galactose, ribose, erythrose, etc.), ketoses (inosose, fructose), disaccharides (sophorose, maltose, cellobiose, and melibiose). The oxidation of aldohexoses involves mainly elimination of $C_{(1)}$ with formation of the corresponding aldopentoses. These are accompanied by a certain quantity of epimerisation products and a mixture of C_{6-3} acids. Results of the oxidation of 3-*O*-methyl-D-glucose and of rhamnose indicate that this reaction may be of preparative value, e.g. for the synthesis of *O*-methylpentoses or deoxypentoses. Disaccharides react similarly: hexosylhexoses give hexosylpentoses. Interesting results have been obtained for the oxidation of D-fructose[309]: the manganese dioxide reacts with the carbonyl group adjacent to the first carbon atom of D-fructose with the formation of the 2-oxo-D-arabinoaldohexose, but with inadequate selectivity.

Manganese dioxide has been used in aqueous medium for the oxidation of derivatives of nucleic acids and similar compounds. Thymidine 5′-phosphate[310], adenine, 6-methylaminopurine, guanine, and 9-ethylguanine[311] have been subjected to oxidation. The latter compounds are oxidised fairly rapidly, products of the degradation of the purine ring — urea, alkylureas, guanidine, biuret, etc. — being formed. Purine nucleosides — adenosine and guanosine — are oxidised rather more slowly. Pyrimidine nucleosides — uridine, cytidine, and thymidine — remain unchanged during the same conditions.

The present review shows that during recent years active manganese dioxide in its various modifications has been finding ever wider use for numerous reactions of an oxidising character involving diverse classes of organic compounds.

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